



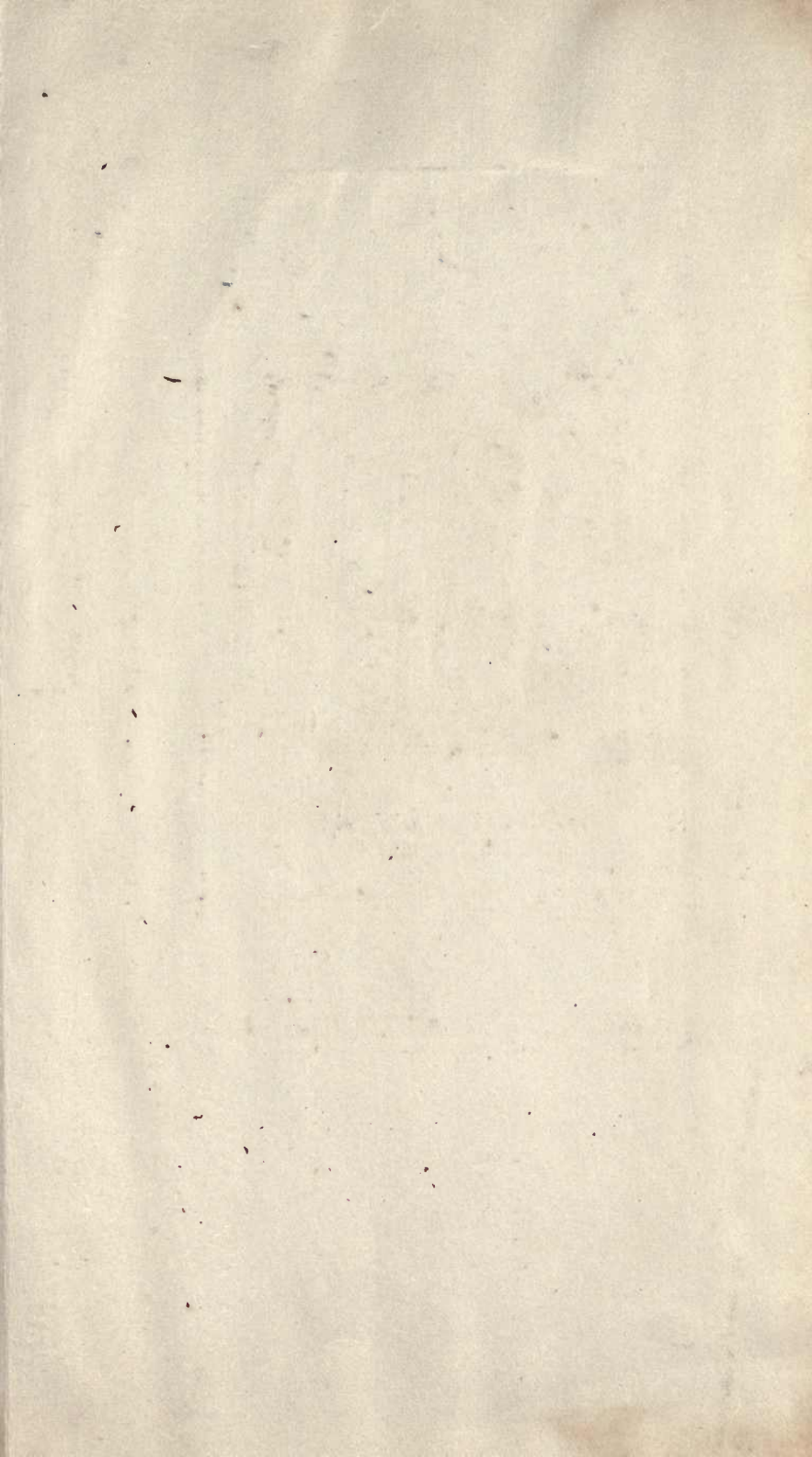
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# LECTURES ON EXPLOSIVES.

*A COURSE OF LECTURES*

PREPARED ESPECIALLY AS

A MANUAL AND GUIDE

IN THE LABORATORY OF THE

U. S. ARTILLERY SCHOOL.

BY

WILLOUGHBY WALKE,

*First Lieutenant, Fifth United States Artillery,*

INSTRUCTOR.

*SECOND EDITION, REVISED AND ENLARGED.*

FIRST THOUSAND.



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## PREFACE TO THE FIRST EDITION.

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THE following course of lectures is intended to serve as a manual and guide in the practical laboratory-work in the course of explosives at the U. S. Artillery School.

The aim has been to present the subject systematically and logically, due consideration being given to the sequence in which the various classes of explosives are arranged, so that a certain degree of familiarity may be acquired in manipulating the less sensitive and dangerous mixtures before undertaking experiments with the high explosives.

Particular attention has been given to the *service tests* of the various explosives, in the description of which all technical terms have been avoided as far as possible.

While the bulk of the matter here presented is the result of compilation, it is believed that a portion at least appears in print for the first time.

In submitting these pages I wish to acknowledge my indebtedness for assistance and encouragement to Professor Munroe, and Lieutenant-Colonel R. T. Frank, 2d Artillery, Commandant of the Artillery School.

With the permission of Professor C. E. Munroe, Chemist to the U. S. Navy Torpedo Corps, I have borrowed largely from his course of "Lectures on Chemistry and Explosives," delivered at the Torpedo Station, the arrangement of the subject-matter being slightly changed to meet the requirements of the Artillery School.

WILLOUGHBY WALKE,  
*1st Lieut., 5th Artillery.*

U. S. ARTILLERY SCHOOL,  
FORT MONROE, VA., November, 1891.



## PREFACE TO THE SECOND EDITION.

---

IN preparing the present edition of "Lectures on Explosives" the same general outline of the previous edition has been followed.

The subject-matter has been enlarged, and it is believed that the value and usefulness of the work have been considerably increased not only as a text-book but for purposes of reference.

In addition to those friends who aided me in the preparation of the earlier edition I wish to acknowledge my indebtedness particularly to M. Berthelot, Membre de l'Institut, President de la Commission des Substances, Explosives, etc., with whose permission I have borrowed Chapter II. from his work "Sur la Force des Matières Explosives d'après la Thermo-chimie"; and John W. Mallet, Professor of General and Industrial Chemistry in the University of Virginia.

WILLOUGHBY WALKE,  
*1st Lieut., 5th Artillery.*

U. S. ARTILLERY SCHOOL,  
FORT MONROE, VA., May, 1897.









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# LECTURES ON EXPLOSIVES.

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## LECTURE I.

### GENERAL CONSIDERATIONS AFFECTING EXPLOSIONS AND EXPLOSIVES.

**Explosive Reactions.**—All chemical changes, whether of combination or decomposition, are called reactions.

Reactions take place in or between molecules. The same atoms are found after a reaction as were present before, but differently arranged or united, forming molecules, different from those which entered into the reaction. The reaction, then, is a change in the manner in which the attractions or affinities of the atoms are exerted. The operations of these attractions are governed by the circumstances under which they are exercised. Then, in order to produce any desired results, certain necessary conditions must be fulfilled.

These conditions vary between extreme limits. Thus, in one compound, the attractions which bind together its parts may be so feebly exercised that the slightest change in its surrounding circumstances will bring about its decomposition, while to reverse those of another compound may require that the most powerful agencies should be exerted for a long time.

Again, compounds which are stable at the ordinary temperature may be broken up when moderately heated, or reactions which occur at the ordinary pressure may be entirely altered if the same materials are brought together at a different pressure.



Reactions may go on rapidly or slowly, and be accompanied by evolution of gas, heat, light, electricity, etc. When these accompaniments are of a certain kind explosive effect results, and we have *explosive* reactions; but such chemical changes are governed by the same laws as all reactions.

The term *explosion* may be considered synonymous with explosive reaction, and may therefore be defined as a chemical reaction causing the sudden or extremely rapid formation of a very great volume of highly expanded (or heated) gas. This development of expansive force characterizes all explosives, and any satisfactory explanation of the phenomena attending an explosion involves the consideration of the chemical and physical conditions prevailing before, during, and subsequent to the reaction.

**The Chemical Composition of Explosives.**—Provided the explosive contain sufficient oxygen to convert all the elements involved into their most stable compounds, or, as more commonly expressed, to produce complete combustion, the products of explosion may be predicted. This is also true of certain binary compounds, but in the case of ternary compounds, and substances deficient in oxygen, the products of explosion not only cannot be predicted, but will vary with all the circumstances and conditions of explosion, such as the method of producing explosion, temperature, pressure, expansion, etc., and must be determined in each instance by careful analysis.

In every explosion, however, the products of the reaction are formed strictly according to the chemical laws governing the affinities of the several elements, and were it not for extraneous circumstances these products would correspond to those due to the maximum heat evolved.

**The Origin of Explosive Reactions.**—Explosive reactions may be brought about in several ways. Generally speaking, anything that will cause the ignition of a combustible body will, when applied to an explosive, cause an explosive reaction, or explosion. In other words, such reac-



tions originate in *heat*, each explosive substance having a specific exploding point to which the temperature of one or more of its molecules must be raised before the reaction resulting in the decomposition of the entire mass can result.

The heating of the initial molecule to the exploding point of the substance is not of itself sufficient to cause the explosion of the entire mass, but this temperature must be transferred without loss by radiation, conduction, expansion, etc., to the adjacent molecules throughout the substance.

This property, possessed by all explosives, involves the question of molecular velocity, which must not be confounded with the rapidity of propagation of the reaction which determines the character of the reaction, whether simple combustion, explosion, or detonation. The molecular velocity of explosive reactions is a function of the temperature, and of the condensation of the substance.

The following are the principal methods of originating an explosion :

1. Contact with a heated body, either solid, liquid, or gaseous.
2. Friction.
3. Percussion.
4. Concussion.
5. Electric spark.
6. Electric current.
7. Thermal radiations.
8. Chemical changes.
9. Physical changes.
10. Chemical and physical changes.

**The Propagation of Explosive Reactions.**—An explosive reaction once begun is propagated throughout the mass of the substance, the phenomenon being reproduced from molecule to molecule. The rapidity with which this propagation proceeds determines the nature of the resulting phenomenon, and varies from the rate of ordinary combustion to the almost infinite velocity of detonation. The velocity of

propagation in the case of the explosion of gunpowder has been measured and determined to vary with the pressure of the surrounding gas. Thus in a vacuum gunpowder cannot be exploded, whereas in the bore of heavy guns the velocity of propagation is about 13 feet per second. In the open air the same velocity is approximately 4 feet per second, and diminishes with every diminution of pressure.

In the case of "low" explosives, the laws of chemical action afford explanation of the phenomena resulting from their decomposition and the propagation of the reaction. This is not true, however, with regard to the modern "high" explosives, as will be shown later.

The influence of pressure has been alluded to in the case of gunpowder; the rate of propagation, however, is subject to other considerations, and may be made to vary in accordance therewith, with the results before mentioned.

Moreover, the same explosive may be made to develop any of these phenomena by varying the physical or mechanical condition of the explosive itself, the external conditions, and the method of initial inflammation.

**Influence of Physical or Mechanical Condition of the Explosive.**—Many instances may be given indicating the influence of its state upon the explosion of a substance. Thus nitroglycerine at temperatures above 40° F. is a liquid, and in the liquid condition may be violently exploded by a fuse or exploder containing fifteen grains of fulminating mercury. Below 40° it freezes and cannot be so fired.

The advantage of dynamite over liquid nitroglycerine lies altogether in the fact that the former contains the explosive body in another mechanical condition, more convenient and safer to use than the liquid form.

The nitroglycerine itself is the same chemically in either case.

The same mixture of charcoal, sulphur, and saltpetre gives a very different effect if made up into large grains than if made up into small ones.

Guncotton presents the most marked example of the

effect of mechanical state, since it can be prepared in so many ways. If flame is applied to loose, uncompressed gun-cotton, it will flash off; if the guncotton is spun into threads or woven into webs, its rate of combustion may be so much reduced that it can be used in gunnery or for a quick fuse; powerfully compressed and wet, it burns slowly; dry gun-cotton may be exploded by a fulminate exploder; wet gun-cotton requires an initial explosion of a small amount of the dry, etc.

**Influence of External Conditions.**—Confinement is necessary to obtain the full effect of all explosives. The most rapid explosion requires a certain time for its accomplishment. As the time required is less, the amount of confinement necessary is less. Then with the sudden or violent explosives the confinement required may be so small that its consideration may be practically neglected. For instance, large stones or blocks of iron may be broken by the explosion of nitroglycerine upon their surfaces in the open air. Here the atmosphere itself acts as a confining agent. The explosion of the nitroglycerine is so sudden that the air is not at once moved.

Again, chloride of nitrogen is one of the most sudden and violent of all explosives. In its preparation it is precipitated from a watery liquid, and therefore is, when used, wet or covered with a very thin film of water.

This thin film of water, not more than  $\frac{1}{1000}$  of an inch in thickness, is a necessary and sufficient confinement, and if it is removed the explosive effect is much diminished. Gunpowder, on the other hand, requires strong confinement, since its explosion is comparatively slow. Thus in firing a large charge of gunpowder under water, unless the case is strong enough to retain the gases until the action has become general, it will be broken, and a large amount of the powder thrown out unburned. This is often the case in firing large-grained powder in heavy guns. The projectile leaves the gun before all the powder has burned, and grains or lumps of it are thrown out uninjured.



The confinement needed by the slower explosives may be diminished by igniting the charge at many points, so that less time is required for complete explosion.

**Influence of Method of Initial Inflammation.**—In any explosive reaction, the mode of bringing about the change exercises an important influence. The application of heat, directly or indirectly, is the principal means of causing an explosion. Thus, in gunnery, the flame from the percussion-cap or primer directly ignites the charge; so also a fine platinum wire heated by an electric current will ignite explosive material which is in contact with it. Friction, percussion, concussion, produce the same effect indirectly, by the conversion of mechanical energy into heat, which is communicated to the body to be exploded.

When one explosive body is used as a means of firing another, it may be considered that the blow delivered by the gas suddenly formed from the firing-charge acts percussively upon the mass to be exploded. The particles of this gas are thrown out with great velocity, but meeting with the resistance of the mass around them they are checked, and their energy is converted into heat. It is found, however, that the action of explosives on one another cannot be perfectly explained in this way.

If the action were simply the conversion of energy into heat, then the most powerful explosive would be the best agent for causing explosion. But this is not the case. Nitroglycerine is much more powerful than fulminating mercury; but fifteen grains of the latter will explode guncotton, while seventy times as much nitroglycerine will not do it.

Chloride of nitrogen is much more violent than fulminating mercury, but larger quantities of the former than of the latter must be used to cause other explosions.

Again, nitroglycerine is fired with certainty by a small amount of fulminating mercury, while with a much larger amount of gunpowder the explosion is less certain and feebler.

In these cases it is evident that the fulminating mercury must have some special advantage, since it produces the de-

sired effect more easily than the others. It may be considered that the fulminating mercury sets up a form of motion or vibration to which the other bodies are sensitive. Just as a vibrating body will induce corresponding vibrations in others, so the peculiar rate of motion, or wave of impulse, sent out by fulminating mercury, exerts a greater disturbing influence upon the molecules of certain bodies than that derived from other substances.

An explosive molecule is unstable and very susceptible to external influences. Its atoms are in a nicely balanced state of equilibrium, which is, however, more readily overturned by one kind of blow than another. The explosive molecule takes up the wave of impulse of the fulminate, but the strain is too great, and its own balance is destroyed.

In addition, the explosion proceeds very differently when brought about in this way than when caused by simple inflammation. When a mass of explosive is ignited by a flame, the action extends gradually through it; but if it is exploded by a blow, acting in the manner above described, it is plain that the explosion will be nearly instantaneous throughout, since the impulse will be transmitted through the mass with far greater rapidity than an inflammation proceeding from particle to particle. The explosive reaction will then proceed much more rapidly, and the explosive effect will be much sharper, that is, more violent.

**Combustion, Explosion, Detonation.**—These terms are used to express different phases of the same reaction, depending almost altogether upon the velocity of propagation of the explosive reaction. This may be considered absolutely true with regard to the first two phenomena. In the case of combustion the reaction progresses very slowly and gradually, and can be controlled by mechanical means, such as comminuting the particles, etc., while in the case of explosion the velocity of propagation is relatively very rapid, and the true nature of the changes that occur is frequently lost sight of on account of the rapidity with which the different phases of the phenomenon succeed each other. There can be no doubt,

however, that explosion is but a rapid form of combustion.

In the case of detonation, the laws governing chemical action fail to account for all of the phenomena accompanying the explosive reaction in which the time element is reduced to the minimum, and the theory of thermodynamics must be applied in order to afford a satisfactory explanation.

Thus in the case of mercury fulminate, which is peculiarly effective in provoking detonation, the decomposition of this substance is characterized by extremely rapid chemical transformation and intense local action. We may assume, therefore, that the energy of the initial shock produced locally by this substance is transformed into heat at the point of action which serves to raise the temperature of the particles (or molecules) first subjected to its action up to their point of explosive reaction. The sudden decomposition of these particles produces a second shock more violent and energetic than that received, which is in turn transmitted, thus developing a regular succession of shocks and decompositions which is propagated throughout the entire mass from particle to particle with a velocity far greater than that characterizing simple inflammation.

According to this view, detonation is the result of a combination of true chemical and dynamical reactions, neither of which alone suffices to explain the attending phenomena. If the transformation were due merely to the mechanical energy of the particles of gas liberated at the initial shock at a tremendous velocity being converted into heat by impact against the mass of the explosive substance, then it would follow that the most powerful explosive would be the best detonating agent; that is, however, by no means the case, for a few grains of fulminate of mercury in a metal tube will detonate guncotton, whereas nitroglycerine, although possessed of more explosive force, will not do so unless used in large quantities. The fact of its being possible to detonate wet guncotton is also a proof that the action cannot be due to heat alone.



As already stated, an explosive molecule is most unstable, certain very delicately balanced forces preserving the chemical and physical equilibrium of the compound.

If these forces be rapidly overthrown in succession, we have explosion; but when, by a blow of a certain kind, they are instantaneously destroyed, the result is detonation. Just as a glass globe may withstand a strong blow, but be shattered by the vibration of a particular note, so it is considered by some authorities that, in the instance cited, the fulminate of mercury communicates a vibration to which the guncotton molecule is sensitive, and which overthrows its equilibrium; it is not sensitive to the vibrations caused by nitroglycerine, which only tears and scatters it mechanically. Although the action of detonation has been spoken of as instantaneous, and may practically be so considered, yet a certain infinitesimal duration of time is required for the metamorphosis; different substances possess, doubtless, different rates of detonation, for we can scarcely conceive of a mechanical mixture, such as gunpowder, being so sensitive to the action of the detonating impulse as a definite chemical compound, and the rate even varies slightly, for the same explosive, with its chemical state. It has been shown by means of Captain A. Noble's chronoscope that compressed guncotton, when dry, is detonated at a velocity of from 17,000 to 18,000 feet a second, or about 200 miles a minute; by using a small primer of dry guncotton the same substance in the wet state may be detonated at the increased rate of from 18,000 to 21,000 feet a second, or about 240 miles a minute.

**Bodies Susceptible of Detonation.**—Some substances seem always to detonate no matter how fired (e.g., chloride of nitrogen, the fulminates, etc.), while others are detonated or not according to the mode of firing (e.g., guncotton, gunpowder, etc.).

Probably all explosives can be detonated if the right methods of doing so are known.

Guncotton seems to have a greater range of susceptibility

to different modes of firing than any other explosive agent. It can be made to burn slowly without explosion, and the rapidity of its action can be increased up to the detonating point.

Nitroglycerine always explodes powerfully, but its effect is much lessened when fired with gunpowder.

Gunpowder as ordinarily used is, of course, not detonated, as the violent, sudden effects of detonation would be undesirable. For other purposes (e.g., torpedoes, blasting, etc.) it would be a great advantage if it could be made to give more violent explosive effects by a peculiar mode of firing. It has been demonstrated that this can be done, although the best mode of doing it, or whether detonation is actually accomplished, is not known. Experiments in this direction can hardly fail to give valuable results.

Probably a mechanical mixture like gunpowder can never be brought by any mode of firing to approach as near to a perfect detonation as the chemical substance nitro-glycerine or guncotton; but even if not detonated, better effects for certain uses may be obtained from it if the proper means are used.

Roux and Sarrau have recently published some interesting results of experiments on the different explosive effects produced by some bodies by certain modes of firing. They divide explosions into two kinds: detonations, or *explosions of the first order*, and simple explosions, or *explosions of the second order*. Simple explosions are produced either by direct inflammation or by a small charge of gunpowder. Detonations are obtained from nitroglycerine, guncotton, picric acid, and certain picrates by exploding with fulminating mercury.

Fulminating mercury, they state, does not detonate gunpowder; but if the exploding charge is a small amount of nitroglycerine, itself detonated by fulminate, an explosion of the first order is obtained from gunpowder. The relative effects were approximately measured by determining the



quantities necessary to rupture small cast-iron shells of nearly equal strength.

The following are among the results given, showing the great difference in force of the two kinds of explosion:

	Explosive Force.	
	First Order, or Inflammation.	Second Order, or Detonation.
Nitroglycerine .....	4.80	10.13
Guncotton (compressed) .....	3.00	6.46
Picric acid ..	2.00	5.50
Potassium picrate.....	1.80	5.30
Gunpowder.....	1.00	4.34

There is for each explosive about a certain amount and kind of force required to effect detonation, which must not be materially departed from.

If the exploder is too weak, inflammation or a feeble explosion only will result; if too heavily charged, it is more likely to scatter or disintegrate the material acted upon than to explode it. There is also a relation between the mass of the explosive and the charge of the detonator which must be observed. This relation is more marked with some explosives than with others. Thus, nitroglycerine is a body easily detonated, and the same amount of fulminate seems to fire equally well all usual quantities. If a single particle is detonated, the action quickly extends through the whole mass.

Other substances, less easily detonated, require that as the mass is increased the force applied shall be increased, so that all the particles shall receive a sufficient blow, otherwise only a part will be detonated.

#### PRODUCTS OF EXPLOSIVE REACTIONS.

The products of the reaction which characterizes an explosion are, first, *gas* or *gases rapidly formed*, and, secondly, *heat evolved* which serves to expand and further increase the volume of gas.



The effects produced by an explosion are made evident by the pressure exerted by the gases, and by the work accomplished.

The first effect is due to the gas or gases evolved, and depends upon their volume and pressure; the second, however, is a function of the heat liberated, which measures the energy developed.

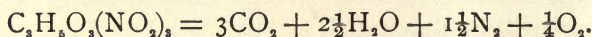
To define the force of an explosive, however, there is still another factor to be considered, and that is *the rapidity of the reaction*; these three elements, the volume of gas, the quantity of heat, and the rapidity of the reaction, afford all the data necessary to calculate the force of an explosive.

**The Volume of Gas Evolved.**—The volume of gas evolved in any explosive reaction may be measured directly by means of various apparatus, based upon either static or dynamic laws. The apparatus involving the static method are known as pressure-gauges, such as Rumford's, Rodman's cutter gauge, Uchatins' eprouvette, and various crusher gauges.

The dynamic method employs the various ballastic pendulum apparatus, crushing tests, etc.

These methods will be referred to later.

The volume of gas may also be closely calculated, but only when they are simple and stable products, such calculations being made at 0° C. and 760 mm. Thus let it be required to determine the volume of gas evolved by one molugram\* of nitroglycerine. The explosive reaction of nitroglycerine may be represented by the equation



By weight,

$$227 = 132 + 45 + 42 + 8.$$

By volume,

$$2 = 3 + 2\frac{1}{2} + 1\frac{1}{2} + \frac{1}{4}.$$

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\* A molugram is the weight of a substance (expressed in grammes) equivalent to its molecular weight.

The weights of the several products of the above reactions are calculated by multiplying their specific gravities by the weight of one litre of hydrogen at  $0^{\circ}$  C. and 760 mm. (0.0896 gm.). Thus,

$$\begin{aligned}\text{One litre of CO}_2 &= 22 \times .0896 = 1.9712 \text{ gm.} \\ \text{" " " H}_2\text{O} &= 9 \times \text{"} = 0.8064 \text{ " } \\ \text{" " " N}_2 &= 14 \times \text{"} = 1.2544 \text{ " } \\ \text{" " " O}_2 &= 16 \times \text{"} = 1.4336 \text{ " }\end{aligned}$$

The volume of permanent gases at  $0^{\circ}$  and 760 mm. is constant, and, assuming the gramme as the unit of mass, is found to be 22.32 litres. Thus,

$$\begin{aligned}\text{Vol. of 44 gm. of CO}_2 \text{ at } 0^{\circ} \text{ C. and 760 mm.} &= \frac{44}{1.9712} = 22.32 \text{ litres.} \\ \text{" " 18 " " H}_2\text{O " " " " " " " } &= \frac{18}{0.8064} = 22.32 \text{ " } \\ \text{" " 28 " " N}_2 \text{ " " " " " " " } &= \frac{28}{1.2544} = 22.32 \text{ " } \\ \text{" " 32 " " O}_2 \text{ " " " " " " " } &= \frac{32}{1.4336} = 22.32 \text{ " }\end{aligned}$$

Therefore,

$$\begin{aligned}132 \text{ gm. of CO}_2 \text{ at } 0^{\circ} \text{ C. and 760 mm.} &= 22.32 \times 3 = 66.96 \text{ litres.} \\ 45 \text{ " " H}_2\text{O " " " " " " } &= 22.32 \times 2\frac{1}{2} = 55.80 \text{ " } \\ 42 \text{ " " N}_2 \text{ " " " " " " } &= 22.32 \times 1\frac{1}{2} = 33.48 \text{ " } \\ 8 \text{ " " O}_2 \text{ " " " " " " } &= 22.32 \times \frac{1}{4} = 5.58 \text{ " } \\ &\hline &161.82 \text{ " }\end{aligned}$$

Therefore one molugram, or 227 gm., of nitroglycerine when exploded produces 161.82 litres of gas at  $0^{\circ}$  C. and 760 mm. To determine the volume of gas at the temperature of explosion, we simply apply the Law of Charles,\* thus:

$$V : V' :: T : T', \text{ or } V' = V \frac{T'}{T},$$

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\* According to the Law of Charles, the volume of any gas varies directly as its temperature on the Absolute Scale, provided the pressure remains constant. Knowing the temperature on the Centigrade Scale, the corresponding temperature on the Absolute Scale is obtained by adding 273 to the degrees C.

in which  $V$  represents the original volume;

$V'$  represents the new volume;

$T$  represents the original temperature on the absolute scale;

$T'$  represents the new temperature on the same scale.

In the present case  $T' = 6001^{\circ}$ .

Therefore substituting, we have

$$V' = \frac{161.82 \times 6001}{273} = 3557 \text{ litres.}$$

Or at the temperature of explosion one molugram of nitroglycerine produces 3557 litres of permanent gas. The volume of gas thus calculated when measured by the apparatus referred to is generally recorded in terms of the pressure exerted, and, notwithstanding the great difficulties attending such investigations, the calculated and recorded results have been found to agree within reasonable limits.

Thus M. Berthelot measured by means of his crusher gauge the pressure developed by the explosion of 10 gm. of mercury fulminate, and found it to be 1183 kgm. per sq. cm. By calculation it should be 1293 kgm. per sq. cm. In the case of nitrogen sulphide (by the same investigator) the result was as 1703 to 1707 kgm. per sq. cm.

**Temperature of Explosion.**—The temperature of explosion which serves to expand these gases may also be measured directly by means of the calorimeter, or calculated theoretically.

The measurement of such high temperatures as obtain at the instant of explosion, however, is attended with so many difficulties that that method is limited practically to a very few special experimenters.\*

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\* M. Berthelot has performed the most notable experiments in this direction, and the results of his labors afford the most complete and reliable data to be had on the subject. These results will be found tabulated in his work "Sur la force des matières explosives d'après la Thermo-chimie."



The temperature of an explosive reaction may be calculated by the formula

$$T = \frac{WC}{W_1S_1 + W_2S_2 + W_3S_3 + \text{etc.}},$$

in which  $T$  = the temperature sought;

$W$  = the weight of explosive used;

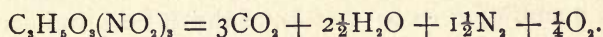
$C$  = the calorific power of the explosive at  $100^\circ \text{C}$ ;

$W_1, W_2, W_3$  = the weights of the products of explosion;

$S_1, S_2, S_3$  = the specific heats\* of the products of explosion.

Thus let it be required to calculate the temperature developed by the explosive reaction of one gramme of nitroglycerine.

The equation representing such reaction may be written as follows:



According to Berthelot, the calorific power of nitroglycerine is 356,500 cal.† Substituting in the formula above this value for  $C$ , and for  $W_1S_1, W_2S_2, W_3S_3$ , etc., their values as follows:

$$\begin{array}{rcl} W_1S_1 & = & 132 \times .2169 = 28.63 \\ W_2S_2 & = & 45 \times .4805 = 24.63 \\ W_3S_3 & = & 42 \times .2438 = 10.24 \\ W_4S_4 & = & 8 \times .2175 = 1.74 \\ & & \hline & & 62.24 \end{array}$$

we have

$$T = \frac{356500}{62.24} = 5728^\circ.$$

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\* The specific heat of a substance is the amount of heat required to raise *one gramme* of the substance through  $1^\circ \text{C}$ .

† A calorie (cal.) is the quantity of heat required to raise one gramme of water  $0^\circ$  to  $1^\circ \text{C}$ .

A large calorie (Cal.) is the quantity of heat required to raise one kilogramme of water from  $0^\circ$  to  $1^\circ \text{C}$ .

This temperature is theoretically independent of the containing vessel in which the reaction takes place, provided this reaction remains unchanged.

**Effect of Dissociation.**—The calculated temperature of an explosive reaction is as a general rule greater than the actual temperature. In the first place the specific heat of gases under pressure is not constant, but increases with the temperature, so that an equal quantity of heat applied to compressed gases produces a less rise of temperature than would result from constant specific heats of the same gases at normal pressure, which is the assumption in these calculations.

In the second place, the phenomenon of dissociation must be considered in connection with these reactions. All calculations as to the temperature of explosion are based upon the products of the reaction after partial cooling, whereas it is more than probable that at the instant of explosion the temperature may be so excessive as to determine much simpler products, or even to dissociate the mass into its constituent elements. Thus the resulting polysulphide may have been separated into sulphur and monosulphide at the temperature of explosion and recombined during the process of cooling; so also the separation of water-gas into its elements of hydrogen and oxygen.

Dissociation is attended with absorption of heat, and is therefore characterized by diminution of pressure of the gaseous system. It moreover exercises its influence at the first period of expansion, and affects the maximum effort developable by the explosive. As the expansion progresses, as in acting upon a projectile in the bore of a gun, the temperature of the gases decreases, and the elements enter more completely into combination with the formation of more complicated products.

The importance of this factor in influencing an explosive reaction must not be overlooked, and has been made an object of special investigation by those who seek to offer a coherent explanation of all the phenomena incident to an explosion.

**Potential Energy of Explosives.**—The quantity of heat liberated by an explosive is fixed and constant, and can be calculated only when the substance undergoes complete combustion. In the case of incomplete combustion the products of decomposition will vary (as stated before) with the initial method of inflammation, pressure, and other attending circumstances, and the heat cannot be calculated. Since, however, the heat liberated measures the maximum work that can be developed by an explosive under atmospheric pressure, if this quantity of heat be multiplied by 425 (its mechanical equivalent) the resulting product will represent the *potential energy* of the explosive, expressed in kilogrammetres.



## LECTURE II.

### PRINCIPLES OF THERMOCHEMISTRY AS APPLIED TO EXPLOSIVES, AND THE CLASSIFICATION AND COMPOSITION OF EXPLOSIVES.

THE scope of this work does not admit of more than reference to such of the principles of thermochemistry as are necessary to a proper understanding of the theory of explosives and of the rationale of explosive reactions. For those who desire to enter more fully into this important branch of the subject of explosives, reference may be had to the investigations of M. Berthelot.

As the result of these investigations, M. Berthelot bases thermochemistry upon three fundamental principles, molecular work, the calorific equivalence of chemical transformations, and maximum work.

**Molecular Work.**—This principle is stated as follows: The quantity of heat liberated in any reaction measures the sum of chemical and physical work accomplished in this reaction.

Whence it follows that the heat liberated in any reaction is precisely equivalent to the amount of work necessary to restore the bodies to their primitive or initial state, this work being both chemical and physical.

Until comparatively recently it was assumed that every synthetical chemical reaction was attended with evolution of heat, and that whenever the elements composing a body were separated by decomposition heat was absorbed.

This error has been corrected, and, depending upon the principle resulting therefrom, reactions are classified as exo-

thermal or endothermal according as heat is liberated or absorbed. Thermochemistry further divides substances into two corresponding classes, exotherms and endotherms. An *exotherm* is a substance which evolves heat during formation. An *endotherm* is a substance which absorbs heat during formation. This division of explosive substances becomes of great importance in calculating the heat developed by an explosive reaction.

In a general sense the amount of heat absorbed in the formation of an explosive measures its stability, although all endothermous substances are not necessarily unstable.

In accounting for the energy developed by any explosive reaction, Berthelot considers merely the initial and final states, and the quantity of heat liberated is the algebraic sum of the heats involved, which may be positive or negative according to circumstances. It is necessary to take into consideration, however, not only the heat of formation of the explosive and that of decomposition, which at extremely high temperatures involves dissociation, as already stated, but the recombination of the atoms of the several elements to form molecules enters as an important factor. Thus in the explosion of nitrogen trichloride the great energy developed may be accounted for by the fact that, although the heat of formation of the substance amounts to 38,100 cal., the separation of the dissimilar atoms of N and Cl may be accompanied by the absorption of an equal or greater quantity of heat, which serves to neutralize the heat of formation, leaving the heat evolved by the combination of the similar atoms of N and Cl in the formation of the molecules of nitrogen and chlorine available for the development of energy.

**The Calorific Equivalence of Chemical Transformations.**—This is also termed the principle of the initial and final state, and is stated as follows: "If a system of simple or compound bodies, under given conditions, undergo physical or chemical changes capable of bringing it to a new state without giving rise to any mechanical effect exterior to the system, the quantity of heat liberated or absorbed by the

effect of these changes depends solely on the initial and final states of the system. It is the same whatever the nature or the sequence of the intermediate states may be."

An explanation of this principle involves that of molecular work and the principle of energy, while it gives rise to several important subordinate theorems.

It is particularly applicable to explosive reactions giving rise to unknown or but partially known products, and to the products of incomplete combustion. Thus it is only necessary to explode the substance, first in pure oxygen, and then in nitrogen, and to measure the heat liberated in each case. The difference between these figures will express the heat of combustion of the products of the second reaction, which measures the energy available in total combustion.

Another important corollary of this principle establishes the difference between the heat of combustion by free and combined oxygen.

As a result, the imperfectly understood action of certain agents entering into the composition of explosives, known as *oxidizers*, is clearly established.

They are no longer to be regarded merely as magazines of oxygen, for we know that the oxygen forming a part of their composition has lost a part of its energy equivalent to the heat of initial combination, and we must distinguish between the entire amount of oxygen contained and the amount available for oxidation. On the other hand, however, it may happen that the combined oxygen may liberate more heat than the free element, as in the case of potassium chlorate.

**Maximum Work.**—"Every chemical change effected without the intervention of a foreign energy tends towards the production of the body or of the system of bodies liberating the most heat."

This principle results from the observation that the system which has liberated the greatest possible amount of heat no longer possesses in itself the requisite energy to effect further decomposition or transformation, but must invoke the



aid of extraneous force or energy. This force or energy may assume one of the many forms of physical agents or of chemical reactions.

This third principle was deduced by M. Berthelot almost entirely from the experimental study of the phenomena of combination and decomposition ("Essai de Mécanique Chimique"), and by its application all explanation of these phenomena is based upon the accepted physical and mechanical theories of maximum work effected by molecular action.

In all subsequent calculations reference may be had to the exhaustive tables contained in the work on thermochemistry by the same author.

#### CLASSIFICATION AND CONSTITUTION OF EXPLOSIVES.

Although the classification of explosives by Berthelot is of little practical value, it serves to show the unlimited nature of the subject from an abstract point of view.

According to Berthelot ("Sur la force des matières explosives") every system of bodies capable of developing permanent gases, or substances which assume the gaseous state by reason of a reaction, such as water above  $100^{\circ}$  C., mercury above  $360^{\circ}$ , etc., can constitute an explosive agent.

Gases themselves become explosive if they are compressed beforehand, or rather if their volume increases in consequence of some transformation. It is not, however, indispensable that the temperature of the system be raised, although that condition is generally fulfilled, and it tends to increase the effects.

The initial system must, however, be capable of existing by itself, at least for some little period of time; its transformation taking place only when provoked by some external cause, such as friction, ignition, shock, or the intervention of a chemical agent, either causing reactions which are propagated chemically ( $\text{H}_2\text{SO}_4$  in the presence of a mixture of  $\text{KClO}_3$  and organic substances), or causing a sharp shock

which, by its mechanical effects, leads to the production of the explosive wave and detonation in general.

**General List of Explosives.**—As classified by Berthelot, the various explosives are divided into eight distinct groups, as follows:

*First Group.*—Explosive gases, such as—

1. Ozone, hypochlorous acid, the gaseous oxides of chlorine, etc., which detonate under very slight influences, such as slight heating or sudden compression.

2. Various gases formed with absorption of heat, but more stable; gases which detonate neither when heated progressively nor when moderately compressed. They may, however, be detonated by the action of fulminating mercury. Such are acetylene, nitrogen dioxide, cyanogen, etc.

*Second Group.*—Detonating gaseous mixtures, formed by the combination of oxygen or chlorine with hydrogen, and gases or vapors of the hydrocarbons.

*Third Group.*—Explosive inorganic compounds, definite bodies, liquid or solid, susceptible of being detonated by shock, friction, or heat; such as—

1. Nitrogen sulphide, nitrogen chloride, nitrogen iodide, mercury nitrate, and certain other metallic nitrates; the fulminating oxides of gold and mercury.

2. The liquid oxyacids of chlorine and concentrated permanganic acid.

3. The solid salts of ammonium, formed by the oxyacids of chlorine, nitrogen, chromium, manganese, and others.

*Fourth Group.*—Explosive organic compounds, definite bodies, liquid or solid, susceptible of being detonated by shock, friction, or heat; such as—

1. Nitric ethers, properly so called; e.g., nitroglycerine.

2. Nitro-derivatives of the carbohydrates; e.g., cotton, paper, wood, and other various kinds of cellulose.

3. Nitro-derivatives of the aromatic hydrocarbons; e.g., tri-nitro-phenol and its derivatives, nitro-oxyphenol, tetra-nitro-methane, chloro-nitro-methane, etc.

4. Diazo-derivatives, e.g., diazobenzene nitrate and sim-

ilar bodies, nitrolic acids and other poly-nitro-derivatives, nitro-ethane, to which the fulminates of mercury and silver, etc., seem to belong.

5. Derivatives of highly oxygenated mineral acids, such as, on the one hand, nitrites, nitrates, chlorates, perchlorates, chromates, permanganates of organic alkalies; on the other hand, nitrous ethers, perchloric ethers, etc.

6. Explosive derivatives of hydrogen peroxide, ethyl, acetyl, etc., peroxides.

7. Hydrocarbon derivatives of mineral oxides which can be easily reduced, especially the salts of silver and mercury oxides; e.g., silver oxalate, mercury oxycyanide, etc.

8. Hydrocarbon derivatives and other bodies characterized by an excess of energy with relation to their elements, such as metallic acetylides, etc.

*Fifth Group.*—Mixtures of definite explosive compounds with inert substances.

All of the foregoing explosives, solid or liquid, can be mixed with inert materials in order to moderate their action; e.g., dynamite, wet guncotton, camphorated guncotton, etc.

*Sixth Group.*—Mixtures consisting of an explosive oxidizable compound, and a non-explosive oxidizing substance which is used to insure the complete combustion of the former, such as—

1. Guncotton mixed with potassium and ammonium nitrate, potassium picrate mixed with potassium chlorate or nitrate, etc.

2. Mixtures of nitric acid with nitro-compounds; e.g., di-nitro-benzene, nitro-toluenes, picric acid, etc., mixed generally in the form of paste.

3. Mixtures of nitric peroxide and nitro-compounds.

*Seventh Group.*—Mixtures with an explosive oxidizing base.

1. Mixtures consisting of an explosive containing an excess of O, such as nitroglycerine, and an oxidizable substance, such as carbon dynamite.

2. Gum dynamite.



*Eighth Group.*—Mixtures consisting of oxidizable and oxidizing substances, solid or liquid, neither of which is explosive separately. Such are—

1. Black powder formed by mixing sulphur, carbon, and potassium nitrate.

2. Powders formed by mixing hydrocarbon compounds, charcoal, coal, wood, sawdust, various kinds of cellulose, starch, sugar, or by mixing sulphur and metals with metallic nitrates.

3. Liquid or pasty mixtures formed by mixing liquid nitric acid either with a combustible liquid or with a solid substance on which it does not act instantaneously.

4. Mixtures of liquid nitric peroxide with various oxidizable substances, such as carbon bisulphide, petroleum (refined), etc.

5. Mixtures of combustibles and chlorates and perchlorates.

6. Mixtures of combustibles with various supporters of combustion, such as potassium bichromate, chromic acid, oxides of copper, lead, antimony, bismuth, etc.

7. Mixtures of a sulphide, a metallic phosphide, or of analogous binary compounds with another metal capable of displacing the former in gaseous form with the liberation of heat.

**Explosive Mixtures and Explosive Compounds.**—For practical purposes it is more convenient to divide explosives into two general classes, explosive mixtures and explosive compounds, according to the manner in which the constituent elements or substances are associated. These two classes may be further subdivided according to the nature and action of their several ingredients.

**Explosive Mixtures.**—The first class consists of those explosive substances which are merely intimate mechanical mixtures of certain ingredients, and which can be again separated more or less completely by mechanical means, not involving chemical action.

These ingredients do not, as a rule, possess explosive properties in their separate condition. There are some, however, which might almost be classed in both categories; for example, *picric powder* is composed of ammonium picrate and saltpetre, the former of which contains an explosive molecule, but is mixed with the latter to supply additional oxygen and thus increase the force.

If a substance that will burn freely in air, combining gradually with the oxygen of the atmosphere, be ignited in pure oxygen gas, the combustion will be much more rapid, and the amount of heat generated greater than at the ordinary atmospheric pressure. If it be possible to burn the substance in a very condensed atmosphere of oxygen, we can readily imagine the combustion being very greatly accelerated, and therefore increased in violence; this is what is ordinarily effected by an explosive "mixture." A combustible body and a supporter of combustion are brought into extremely close contact with one another by means of intimate mechanical mixture; also, the supporter of combustion, or oxidizing agent, is present in a very concentrated form, constituting what may be termed a magazine of condensed oxygen, solid or liquid. In the case of the explosion of a definite chemical compound, the charge may be considered as the resolution of a complex body into simpler forms; this is not, however, always the case where a mechanical mixture is concerned; gunpowder, for example, may be said to contain two elementary substances, C and S, not in chemical union.

**Explosive Compounds.**—In an explosive "compound" the elements are all in chemical combination, presenting a definite explosive "molecule," which contains, so to speak, both the combustible and the supporter of combustion in the closest possible union; we can therefore understand its action being much more sudden and violent than that of the most intimate mechanical mixture.

For purposes of instruction these two principal classes will be further subdivided as follows:

*Explosive Substances.*

## I. Explosive Mixtures.

1. Explosive Mixtures of the Nitrate Class.
2. Explosive Mixtures of the Chlorate Class.

## II. Explosive Compounds.

## 1. Nitro-substitution Products.

## 2. Nitric Ethers, or Esters.

## A. Guncotton and its Derivatives.

## B. Nitroglycerine and its Derivatives.

*a.* Dynamite with an Inert Base.*b.* Dynamite with a Combustible Base.*c.* Dynamite with an Explosive Base. *$\alpha$ .* Base is an Explosive Mixture. *$\alpha'$ .* Mixture belongs to Nitrate Class. *$\beta'$ .* Mixture belongs to Chlorate Class. *$\beta$ .* Base is an Explosive Compound. *$\alpha'$ .* Compound is a Nitro-substitution Product. *$\beta'$ .* Compound is a Nitric Ester.

## 3. Explosives of the Sprengel Class.

## 4. Fulminates, Amides, and Similar Compounds.

## 5. Smokeless Powders.

Although the lines of division between the various classes as given above are not clearly drawn, and one or more explosives in one class may appear, on account of the nature of their composition or action, to fall under another class, or perhaps to partake of the characteristics of two or more classes, this classification is especially well adapted for practical instruction in the laboratory.

**The Composition of Explosives.**—Any substance containing in itself the necessary elements to produce combustion may under certain conditions give rise to an explosion of a very low order. The prime essentials, therefore, of every



explosive, with very few exceptions which will be treated separately, are a combustible and a supporter of combustion. The nature of the products of explosion differ from the phenomena attending ordinary combustion principally on account of the rapidity with which the reaction is propagated, but, as already stated, the characteristic products of an explosive reaction are gas and heat; therefore those substances which, while undergoing decomposition and recombination, give rise to the greatest volume of gas and the maximum quantity of heat are best adapted to enter into the composition of an explosive. Oxygen has long been regarded as the most energetic supporter of combustion, but for obvious reasons is of practical application only in combination with other elements. The various oxidizable substances used in explosive agents contain generally carbon, hydrogen, nitrogen, sulphur, etc., while the oxidizers appear in the form of the various nitrates, chromates, chlorates, etc., in which the oxygen is held more or less closely in union with other elements.

When explosion takes place the nitrogen parts with its oxygen to the carbon, for which it has a great affinity, forming carbonic acid ( $\text{CO}_2$ ) and carbonic oxide ( $\text{CO}$ ) gases, the combination being accompanied with great generation of heat, and the nitrogen gas is set free. In most explosives there is also hydrogen accompanying the carbon, and by its combustion producing an extremely high temperature; it also combines with part of the oxygen to form water in the form of greatly expanded vapor.

The chief explosive compounds are formed from some organic substance containing carbon, hydrogen, and oxygen, by introducing into it, through the action of concentrated nitric acid, a certain portion of nitric peroxide ( $\text{NO}_2$ ), in substitution for an equivalent amount of hydrogen. A new compound differing outwardly very little, if at all, from the original substance is thus formed, but in a very unstable state of chemical equilibrium, because of the feeble union of the nitrogen and oxygen in the  $\text{NO}_2$  molecule. A slight disturbing cause brings into play the stronger affinity of the carbon and hydro-

gen for the large store of oxygen contained in the new compound.

It is not, however, necessary that a substance should contain the necessary elements to produce combustion in order to be an explosive. Thus the two very unstable and practically useless explosive substances, the chloride and iodide of nitrogen, contain neither carbon nor oxygen; but their great violence is equally caused by the feeble affinity of nitrogen for other elements, large volumes of gaseous matter being suddenly disengaged from a very small quantity of a liquid and solid body respectively. An additional and more satisfactory explanation of the explosive force of these and similarly constituted compounds is to be found in the principles of thermochemistry already alluded to.

### LECTURE III.

INGREDIENTS ENTERING INTO THE COMPOSITION OF EXPLOSIVES, AND SUBSTANCES USED IN THEIR PREPARATION.

**1. Potassium Nitrate** (Saltpetre or Nitre,  $\text{KNO}_3$ ) is found in some parts of India, especially in Bengal and Oude, where it sometimes appears as a white incrustation on the surface of the soil, and is often mixed with it to a considerable depth. The nitre is extracted from the earth by treating it with water, and the solution is evaporated, at first by the heat of the sun and afterwards by artificial heat, when the impure crystals are obtained, which are packed in bags and sent to different countries as *grough* (or impure saltpetre). It contains a quantity of extraneous matter varying from 1 to 10 per cent, and consisting of the chlorides of potassium and sodium, sulphates of potash, soda, and lime, vegetable matter from the soil, sand and moisture. The number representing the weight of impurity present is usually termed the refraction of the nitre, in allusion to the old method of estimating it by casting the melted nitre into a cake and examining its fracture, the appearance of which varies according to the amount of foreign matter present.

Saltpetre also occurs as a saline crust in caverns in some parts of the globe; and in the vicinity of Monclova, Mexico, it is found in great purity in veins or mines.

It exists in certain plants, and is formed spontaneously by the decomposition of animal and vegetable substances when mixed with substances containing potash and kept at an even



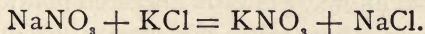
temperature in moist situations. On this principle artificial nitre-beds are made, from which large quantities of nitre are obtained, in France, Germany, Sweden, and Hungary. These beds consist of accumulations of vegetable and animal refuse, to which are added old mortar, limestone, ashes, etc. From time to time stable-drainings are poured over the mass, in which, at an atmospheric temperature of from  $60^{\circ}$  to  $70^{\circ}$  F., the nitrates of the various metals are formed. These nitrates, removed from time to time, and extracted by means of water, consist principally of the salts of potassium, calcium, magnesium, and ammonium, the last three of which may be converted into potassium nitrate by decomposing them with potassium carbonate. The nitrified earth of India yields about one fifth of its weight of nitre; that of the nitre caves from one to ten pounds of nitre to the bushel; while the best nitre-beds afford annually about a quarter of a pound of nitre to a bushel of earth.

Most of the saltpetre used in the United States for the manufacture of gunpowder is obtained from India, whence it is imported in a crystallized state called *crude saltpetre*, containing generally from 15 to 18 per cent of foreign salts, earths, and water. The method of purifying it for use in the manufacture of gunpowder will be described hereafter.

Potassium nitrate is distinguishable by the long striated or grooved six-sided prismatic form in which it crystallizes, and by the deflagration which it produces when thrown on red-hot coals. It fuses at about  $635^{\circ}$  F. to a colorless liquid, which solidifies on cooling to a translucent, brittle, crystalline mass. At red heat it effervesces from the escape of bubbles of oxygen, and is converted into potassium nitrite ( $\text{KNO}_2$ ), which is itself decomposed by a higher temperature, evolving nitrogen and oxygen, and leaving a mixture of potassium oxide ( $\text{K}_2\text{O}$ ) and potassium peroxide ( $\text{K}_2\text{O}_2$ ). In contact with any combustible body it undergoes decomposition with great rapidity, five sixths of the oxygen being available for the oxidation of the combustible substance and the nitrogen being evolved in a free state.

**2. Sodium Nitrate** (Cubical or Chili Saltpetre,  $\text{NaNO}_3$ ). This salt has been proposed as a substitute for potassium nitrate in the manufacture of gunpowder, but, on account of its hygroscopic properties, it has never been adopted, since gunpowder made with it would, under ordinary conditions, soon become useless from moisture absorbed from the atmosphere. In a hot, dry climate sodium nitrate powders, if made only a short time before being required for use, would be valuable, and cheaper than ordinary gunpowder, and such powders were largely used in the construction of the Suez Canal, and continue to be used for blasting in mines. Absolutely pure sodium nitrate is said to be not unduly deliquescent, but the material as found in commerce contains other salts which are supposed to induce this property, and are difficult to remove by any reasonably economical process.

The salt is, however, indirectly largely and increasingly used in the manufacture of gunpowder, for by the simple process of boiling it with potassium chloride it is converted into  $\text{KNO}_3$ , which is retained in the hot solution while sodium chloride is deposited—



Practically the method adopted is to add the potassium chloride (now obtained largely from the refuse of beet-root used in sugar-manufacture) to a boiling solution of sodium nitrate, removing the sodium chloride formed by means of a perforated ladle, and allowing the suspended impurities to settle. The supernatant liquid is then run into crystallizing pans, and the potassium nitrate is deposited.

As an oxidizing agent sodium nitrate contains more available oxygen than the potassium salt, but at very high temperatures it exercises a less powerful oxidizing action upon combustible bodies.

Sodium nitrate, as its commercial name, *Chili saltpetre*, indicates, is found in vast quantities in Chili (especially in the districts of Tarapaca and Atacama), where in its crude state it is known as *caliche*. The crude salt contains as impurities

sodium chloride and various other salts, sand, clay, etc. On account of the form in which it crystallizes, rhombohedra, this salt is also called *cubical saltpetre*.

**3. Ammonium Nitrate.**—Ammonium nitrate is very sparingly found in nature, but is readily prepared artificially. In small quantities it can be made by neutralizing nitric acid with ammonium carbonate and evaporating the solution until the surface of the solution is covered with a thin crystalline layer of the salt, and then allowing the bulk of the nitrate to crystallize out, which it does in the form of large columnar crystals, not unlike those of potassium nitrate, having a bitter saline taste.

A method has been patented (Benker) involving the double decomposition of sodium nitrate and ammonium sulphate. These salts are dissolved, and a mixture of the two solutions is submitted to a temperature ( $-15^{\circ}\text{C.}$ ) at which the ammonium nitrate will freeze and separate out, while the sodium sulphate remains in solution.

Commercially, however, it is prepared by causing ammonium sulphate and lime to react with the aid of heat, and absorbing the ammonia gas thus liberated in dilute nitric acid.

Like all ammonium salts, the nitrate, when heated (especially if previously moistened with potassium or sodium hydrate), evolves ammonia gas and becomes acid. It melts at  $100^{\circ}\text{C.}$ , and is completely decomposed at  $200^{\circ}\text{C.}$ , with the formation of  $\text{N}_2\text{O}$ . Ammonium nitrate is highly hygroscopic, rapidly becoming liquefied upon exposure to the atmosphere. When dissolved in water, the act of solution is attended with considerable absorption of heat, and this property is utilized in many so-called freezing-mixtures.

Ammonium nitrate has recently attracted considerable attention as one of the substances investigated with the object of obtaining a base for one class of smokeless powders. But on account of its great hygroscopicity it has been practically abandoned as an ingredient for military powders.

**4. Barium, Lead, and Strontium Nitrates** ( $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ).—These salts have been experimented



with as oxidizers in various powders, but, with the exception of barium nitrate powder, none of them have ever attained a commercial value, and that one has almost entirely disappeared except as a relic of the past.

*Barium Nitrate* has been substituted principally to produce a slower-burning powder, but the increased weight of the powder resulting from such a substitution is a serious objection. For instance, the chemical equivalent of  $\text{KNO}_3$ , being 101, and that of  $\text{Ba}(\text{NO}_3)_2$ , 130.5, the latter salt increases by one third the weight of the oxidizing agent necessary to consume a given weight of the combustible. The salt is prepared by dissolving the native carbonate in nitric acid, filtering the solution, and evaporating. It crystallizes in transparent, colorless octahedrons, which are anhydrous. They require for solution 8 parts of cold and 3 parts of boiling water.

*Lead Nitrate* is prepared by dissolving finely ground litharge (lead carbonate) in dilute nitric acid, allowing the solution to settle, and decanting the clear supernatant liquid, from which the nitrate crystallizes out in white octahedra. It is only slightly hygroscopic, readily decomposed by heat, and for its chemical equivalent (165.5) yields for equal equivalents one fifth more oxygen than the other nitrates. The objections against its use in explosives are first its cost; secondly, the ease with which it decomposes (with reduction of lead to the metallic state), and the gases developed upon decomposition, which are very deleterious. It is therefore used only for very special purposes.

*Strontium Nitrate* demands merely passing mention, its use being entirely limited to pyrotechny to produce a brilliant red flame.

*General Qualitative Tests applicable to all Nitrates.*—1. All nitrates when heated upon charcoal by means of the blow-pipe deflagrate with considerable violence.

2. Dissolve a crystal of ferrous sulphate in a solution of a nitrate. Upon adding carefully a few drops of concentrated sulphuric acid down the side of a test-tube containing the

double solution, a reddish-brown or purple layer will be formed at the junction of the two liquids. (Sometimes the layer is black, due to the formation of an unstable compound having the composition  $2\text{FeSO}_4 \cdot \text{NO}$ .)

3. Introduce into a test-tube containing a nitrate solution a few copper turnings and a few drops of concentrated sulphuric acid. Upon the application of heat, dark reddish-brown fumes of nitrogen peroxide ( $\text{N}_2\text{O}_4$ ) are evolved, which redden but do not bleach litmus-paper.

4. To a solution of indigo add a nitrate solution. No effect is noticed until heat is applied, when the indigo will be bleached.

5. Boil a minute quantity of gold-leaf in hydrochloric acid. Upon the addition of a small quantity of a nitrate solution the gold disappears, to appear again as a purple precipitate (purple of Cassius) upon the addition of the protochloride of tin (solution).

To detect the presence of a nitrate in a suspected solid, place a minute quantity upon a porcelain surface, moisten it with concentrated sulphuric acid, and introduce a minute crystal of brucine. If a nitrate be present, a brilliant-scarlet color will appear.

7. To apply this test (6) to a solution, introduce into a test-tube containing the suspected nitrate a few drops of brucine (1 part of brucine to 300 parts of 5% dilute sulphuric acid). Upon pouring carefully down the side of the test-tube a few drops of concentrated sulphuric acid, a bright-scarlet layer changing to yellow will appear at the line of contact if a nitrate be present.

8. Another delicate test applicable to suspected solids is as follows: Place a minute quantity of the substance supposed to contain a nitrate upon a porcelain surface and moisten it with a drop of concentrated sulphuric acid. Introduce a small quantity of diphenylamine. If a nitrate be present, a deep-indigo color will quickly appear.

9. This test may be applied to a solution supposed to contain nitrate as follows: Introduce into a test-tube con-

taining the solution a few drops of diphenylamine (dissolved in sulphuric acid), and then pour carefully down the side of the test-tube. If a nitrate be present in the solution, a deep-indigo-colored layer will appear along the surface of contact.

10. The presence of a nitrate in solution may also be detected by introducing into the test-tube a few crystals of pyrogallic acid, and then pouring a few drops of concentrated sulphuric acid down the side of the tube. The presence of a nitrate is shown by the appearance of a deep-brown color along the surface of contact.

Tests (6), (7), (8), (9), and (10) are extremely delicate, and since sulphuric acid may contain traces of nitric acid (hydric nitrate), it is necessary to test the sulphuric acid alone in order to determine its purity before using it in these tests.

To determine the base to which a nitrate belongs, it is generally sufficient to apply the test of flame-coloration. Thoroughly clean a loop of platinum wire (by moistening it with strong HCl and heating it intensely until no color is produced in a non-luminous Bunsen flame), dip it into a solution of the nitrate, and introduce the loop into the Bunsen flame again:

1. If the color imparted to the flame be *pale lilac* as seen directly, but changes to *crimson* when viewed through an indigo prism, the base is potassium.

2. If the flame seen directly be *intense yellow*, but fades away or appears *nearly white* when viewed through an indigo prism, the base is sodium.

3. The presence of both potassium and sodium in the same substance may be detected in this way, since the intense yellow will obscure the faint lilac when viewed directly, but the crimson color due to the presence of potassium will predominate when the prism is applied.

4. The coloration produced directly by the barium salt is yellowish green.

5. The coloration due to strontium is deep crimson, both directly and through the indigo prism.



6. The presence of ammonium is readily detected by the evolution of the ammonia gas (detected by its odor), as already indicated.

7. The lead salt is equally easily determined by the reduction of lead to the metallic state upon charcoal before the blowpipe.

Although the flame-colorations will, as a general rule, suffice to determine the base, a more satisfactory though tedious test is that of the spectroscope, which develops the characteristic spectra of each of the several elements.

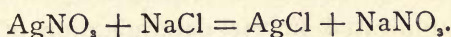
QUANTITATIVE TESTS FOR NITRE.—As has been already stated, the principal impurities contained in nitre are moisture, sand, and organic matter, potassium and sodium chlorides, potassium, sodium, and calcium sulphates, and in that prepared from  $\text{NaNO}_3$ , a little of the latter generally remains. These impurities are estimated as follows:

*Moisture.*—The moisture is determined by weighing 5 gm. in a watch-crystal or porcelain crucible (of known weight), and placing the crystal or crucible in a steam-oven for twenty-four hours. It is then removed from the oven, allowed to cool under a desiccator, and reweighed. The loss of weight is due to the moisture which has been driven off. If calcium or magnesia nitrates are present, one gramme of potassium chromate (neutral) is added to prevent their decomposition.

*Insoluble Matter.*—Treat with water the mass from which the mixture has been eliminated and filter. The difference in weight of the filter before and after (when dry and cool) filtration measures the insoluble matter. Concentrate the filtrate obtained in this manner by evaporating to any volume N. Reserve one third of this solution for the estimation of the chlorides, one third for the sulphates, and one third for calcium salts. Say that the concentrated solution measures 150 c.c.

*Chlorides.*—Fifty c.c. are placed in a clean porcelain dish, about 30 milligrammes of pure potassium chromate are added, and the solution is stirred until the salt is dissolved, coloring the solution distinctly yellow. A centinormal solu-

tion of silver nitrate is prepared by dissolving 1.7 gm. of the salt in one litre (1000 c.c.) of distilled water. Each cubic centimetre of this solution will detect 0.000585 gm. of NaCl.



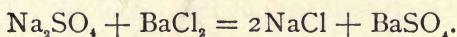
This solution is carefully added from a burette or pipette, graduated to  $\frac{1}{10}$  c.c., the solution being constantly stirred until the red color just begins to be permanent. The amount of silver nitrate solution required is noted. If either the solution of nitre or the silver solution be acid, it must first be neutralized with caustic potash. Suppose 2.6 c.c. of the centinormal silver solution be required; then the weight of NaCl in the nitre is found as follows:

$$2.6 \times 3 \times 0.000585 = 0.004563 \text{ gm.};$$

whence the percentage is calculated by multiplying the latter number by 20; thus:

$$0.004563 \times 20 = 0.09126\% \text{ NaCl.}$$

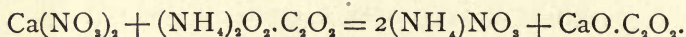
*Sulphates.*—The sulphates are estimated by means of a centinormal solution of barium chloride, prepared by dissolving 2.44 gm. of the crystallized salt,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , in one litre (1000 c.c.) of distilled water. Each c.c. of this solution will detect 0.00174 gm.  $\text{K}_2\text{SO}_4$ , or 0.00142 gm.  $\text{Na}_2\text{SO}_4$ .



Five c.c. of the solution *N* are put into a test-tube, and the  $\frac{N}{100} \text{ BaCl}_2 \cdot 2\text{H}_2\text{O}$  is carefully added by means of a pipette or burette, the amount thus added being carefully noted, and the precipitate thus formed allowed to settle. As soon as the precipitate has entirely subsided, a little more of the  $\frac{N}{100}$  solution is added, and this process is continued until upon the

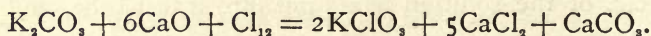
addition of more of the reagent no further precipitate appears. Having thus approximately determined the amount of  $\frac{N}{100}$   $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  required to precipitate, the operation is then continued as indicated in the determination of sulphur in gunpowder, and the exact amount determined. Knowing the number of c.c. required to precipitate all of the sulphates, the weight and percentage of the latter are calculated as in the case of the chlorides.

*Calcium Salts.*—The calcium salts are estimated by means of a centinormal solution of ammonium oxalate, prepared by dissolving 160 grammes of the crystallized salt,  $\text{C}_2(\text{NH}_4)_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , in 1 litre of water. Each c.c. of this solution will detect 0.00164 gm.  $\text{Ca}(\text{NO}_3)_2$ .



The operation in this case is similar in every particular to that used in case of the sulphates, and the final calculations are similar to those adopted in case of the chlorides and sulphates.

**5. Potassium Chlorate ( $\text{KClO}_3$ ).**—This salt, so interesting in its application to the manufacture of explosives, is made commercially by mixing potassium carbonate and lime in the proportions of 1 to 6, and saturating the damp mixture with chlorine. On treating the mass with boiling water a solution is obtained which contains potassium chlorate and calcium chloride; the latter being very soluble remains in the solution, while the  $\text{KClO}_3$  crystallizes out upon cooling. The reaction may be represented as follows:



Potassium chlorate is soluble in about twenty parts of cold and two parts of boiling water; the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles saltpetre. Like the nitrate,  $\text{KClO}_3$  is employed as an oxidizing agent. When heated it gives off the whole of its oxygen and leaves potassium chloride. It deflagrates violently with combustible



matter, explosion resulting from friction or blows, its extreme sensitiveness in this respect precluding its use in the manufacture of gunpowder, although it is used extensively in pyrotechny. The decomposition of  $\text{KClO}_3$  by heat into oxygen and potassium chloride is attended with evolution of heat, one part of the salt producing 39 cal., which, according to the principles of thermochemistry, explains the unusual energy developed by explosives in which this salt enters as an ingredient.

*Qualitative Tests for Chlorates.*—1. Like the nitrates, the chlorates are soluble, and deflagrate when heated on charcoal by means of the blowpipe.

2. Introduce into a test-tube a few small crystals of the salt, and pour upon them a few drops of concentrated sulphuric acid. If a chlorate be present, a brown coloration will result, and upon heating gently an explosion will ensue, with the production of crackling sounds.

(N. B.—Only very minute quantities of the salt should be used, and the mouth of the test-tube should be turned away from the person while making this experiment.)

During this decomposition a greenish-yellow gas, chloric peroxide ( $\text{Cl}_2\text{O}_4$ ), is evolved, which is readily recognized by its suffocating odor.

3. If a cold dilute solution of indigo is gradually added to a *cold* solution of  $\text{KClO}_3$ , so as to color the solution faintly but distinctly blue, and a few drops of concentrated sulphuric acid be added and the mixture be agitated, the color will disappear.

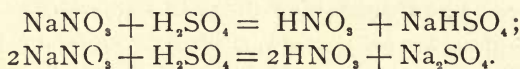
4. A more delicate test, depending upon the action of chlorine upon indigo (bleaching), may be applied as follows: Dissolve a little of the salt in water, and color the solution with a few drops of indigo dissolved in sulphuric acid. Add next a little diluted  $\text{H}_2\text{SO}_4$ , and then drop by drop a solution of sodium sulphite. Immediately the blue color will disappear due to the action of the liberated chlorine, the sulphurous acid depriving the chloric acid of its oxygen.

5. In testing an explosive which is supposed to contain a mixture of chlorates and nitrates, dissolve a small quantity in

warm water and filter. The filtrate will contain the nitrates and chlorates. Introduce a little of the filtrate into a test-tube, add to it a few drops of sulphuric acid, and a small strip of zinc. Heat gently, and add a few drops of silver nitrate. If a chlorate be present a white precipitate of silver chloride will be thrown down.

**6. Nitric Acid** (Hydric Nitrate,  $\text{HNO}_3$ ). — Nitric acid is prepared on a small scale by distilling potassium nitrate with an equal weight of concentrated sulphuric acid. When prepared in large quantities, sodium nitrate, which is cheaper and furnishes a larger proportion of nitric acid, is substituted for the potassium salt.

Either of two reactions may occur:



For practical reasons the first equation represents the relative proportions in which the ingredients are used. The sodium nitrate is introduced into an iron cylinder lined with fire-clay to protect it from the action of the acid, and equal weight of  $\text{H}_2\text{SO}_4$  is poured on it. The furnace in which these cylinders are built (generally in pairs) is then fired up, the nitric acid passes off in vapor, is condensed, and received in stoneware jars.

Thus obtained, nitric acid has a specific gravity of from 1.50 to 1.52, and has a color varying from straw-yellow to reddish yellow, due to the presence of hyponitric acid, although it may be entirely bleached, so as to appear perfectly colorless. Upon exposure to sunlight it is partially decomposed, with the formation of hyponitric acid and water. It is extremely corrosive, staining the skin deep yellow and causing total disorganization. The facility with which nitric acid parts with a portion of its oxygen renders it very valuable as an oxidizing agent, and it is to this property that it owes its importance in its relations to explosives. Comparatively few substances which are capable of forming compounds with oxygen can escape oxidation when treated with

$\text{HNO}_3$ . Its action upon organic substances is most marked, and in many cases the resulting products exhibit a most interesting relation to original substances.

The principal use for nitric acid is the manufacture of the various nitro-compounds, and the nature of its action will be shown later in connection with nitro-substitution products as a distinct class of explosives.

*Tests for Nitric Acid.*—Considered as a true nitrate—hydric nitrate—the several tests enumerated for the nitrates apply equally in the case of nitric acid.

Other special tests to determine the quality of the acid are, however, of great value.

1. The acid should be clear, and the color should not be a deeper yellow than that of a solution of pure picric acid in water.

2. Determine its real specific gravity by weighing in a carefully calibrated specific-gravity bottle at  $15^\circ \text{C}$ ., and comparing the weight obtained with the weight of the same volume of pure distilled water at the same temperature. It should not be less than 1.50 at  $15^\circ \text{C}$ .

3. Ten drops evaporated upon a piece of clean platinum-foil should leave no residue indicative of the presence of *metals*.

4. About 2 c.c. of the acid diluted and put in a test-tube should exhibit no turbidity upon the addition of a few drops of  $\frac{N}{10}$   $\text{HgNO}_3$  solution, indicative of the presence of *chlorine* or *chlorides*.

5. Two c.c. diluted as in (4), and put in a test-tube, should exhibit no turbidity upon the addition of a few drops of  $\frac{N}{10}$   $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution, indicative of the presence of sulphuric acid.

6. The percentage of hyponitric acid present may be determined by titrating with a  $\frac{N}{10}$  solution of potassium permanganate, as follows:



Introduce into a flask a known quantity of  $\frac{N}{10}$  solution of potassium permanganate by means of a burette, and by means of an accurate pipette add 2 c.c. of the nitric acid to be tested, holding the lower end of the pipette immediately over the permanganate solution. Shake the flask, and add a sufficient quantity of the acid to entirely eliminate the color of the solution. Dilute the contents of the flask with distilled water, and add more of the  $\frac{N}{10}$  solution, with frequent agitation, until the contents of the flask retain a *distinct pink* color. Each c.c. of the  $\frac{N}{10}$  solution is equivalent to 0.0046 gm. of hyponitric acid. The weight of hyponitric acid thus found, divided by the specific gravity of the acid being tested and multiplied by 100, will give the percentage of hyponitric monohydrate, which should not exceed 2 per cent in acid used in the manufacture of explosives.

7. The value of nitric acid for the manufacture of explosives may be determined in terms of the percentage of the monohydrate it contains, as follows:

Introduce 2 gm. of the acid under examination into a flask fitted with a ground-glass stopper and having a capacity of not less than 100 c.c. Dilute with distilled water, and titrate with a  $\frac{N}{10}$  solution of sodium hydrate. Each c.c. of such solution is equivalent to 0.0063 gm. of the monohydrate. Either phenol-phthalein or methyl-orange may be used as an indicator. The total number of c.c. of the  $\frac{N}{10}$  solution required indicates the total acidity of the nitric acid, from which the percentage of hyponitric acid must be deducted.

**7. Charcoal.**—Charcoal is described as the residue of the destructive distillation of wood, in which process the hydrogen and oxygen of the wood are for the most part expelled in the forms of wood naphtha ( $\text{CH}_4\text{O}$ ), pyroligneous acid ( $\text{C}_2\text{H}_4\text{O}_2$ ),

carbonic acid, carbonic oxide, water, etc., leaving a residue containing a much larger proportion of carbon than the original wood, and therefore capable of producing a much higher temperature by its combustion with the saltpetre.

The process is conducted in closed iron retorts, the first result being the driving off of the moisture contained in the wood until a temperature of about 284° F. is reached, when the more volatile constituents begin to distil off.

The kind and quantity of charcoal obtainable varies with the kind of wood, although the latter varies also with the temperature and duration of the process of carbonization, diminishing as the temperature increases and increasing directly with the length of time of charring. The percentage of carbon in various charcoals varies almost to as great an extent as the charcoals themselves, and increases with both the temperature and yield.

The physical properties of charcoal also vary between wide limits. Thus, charcoal made at 270° C. is of a brownish-red color, and is slightly friable; that made at about 280° C. is much darker; at 340° C. it becomes black; and all charcoals made at this or higher degrees of temperature are called "black charcoals."

Charcoal made at about 430° C. has a smooth fracture showing the texture of the wood, and may be readily pulverized; that made between 1000° and 1500° C. is very black, very hard and brittle; while above this degree of heat there results a very hard, tough charcoal which emits a ringing metallic sound when struck. The density of charcoal, as well as its hygroscopicity, varies with the temperature of charring, the former diminishing from 1.507 at 150° C. to 1.406 at 290° C., from which point it increases until it reaches 1500° C., where its density is 1.869. It appears that the higher the temperature the less hygroscopic the charcoal, although this point has not yet been absolutely determined.

A very important property of charcoal requires special attention, and that is, the capacity of charcoal to absorb and condense gases on its surface.



The condensation of gases on the surface of charcoal is always attended with disengagement of heat, and if this action be sufficiently rapid and violent it may result in raising the temperature to the ignition point of the charcoal. This actually occurs whenever freshly prepared charcoal is heaped in considerable quantities. The true cause of this phenomenon is as yet unknown.

In recent years a form of charcoal has been used in the so-called brown or cocoa powders which differs materially from that derived from wood. It is made by subjecting rye straw to the action of superheated steam, by means of which all foreign matter is extracted and the carbonization is limited so that the color of the resulting charcoal is that of chocolate.

The rye straw used for this purpose is carefully selected, only thick, heavy stalks being used. The ears, etc., are first removed and the straw is stacked in the open air until thoroughly dry, and is then introduced into the retorts and subjected to the action of superheated steam for several hours.

In the manufacture of brown powders in the United States the DuPont Company uses various forms of carbohydrates. This, however, and the preparation of charcoal for use as an ingredient of gunpowder, will be alluded to later.

*Tests for Charcoal.*—In the laboratory it is only necessary to determine whether the charcoal has been properly charred, and for this purpose it will suffice to estimate the percentage of ash and volatile constituents; incidentally the amount of moisture will become known, and is applied in the subsequent calculations.

1. *Moisture.*—Heat in a drying-oven at  $150^{\circ}$  C. 5 gm. of charcoal previously weighed in a porcelain crucible (of known weight) until the weight becomes constant, allowing the crucible to cool in a desiccator between each weighing. (The temperature of the oven should be raised gradually.)

2. *Ash.*—Ignite to constant weight 5 gm. of charcoal similarly weighed in a tared crucible; the difference in weight will be the ash, whence the percentage becomes known.



3. *Volatile Constituents*.—Place the crucible containing the charcoal from which the moisture has been expelled in a clay crucible, surround the latter crucible with charcoal, and gradually heat it until its sides glow brightly, and maintain this degree of heat for half an hour. Remove, allow to cool, and reweigh the porcelain crucible. The loss of weight will be due to expulsion of the volatile constituents.

8. **Sulphur.** (S).—Until recently all of the sulphur used in the manufacture of gunpowder came from Sicily, where it occurs naturally in a limestone formation, the mineral as it appeared in the mine containing from 6 to 25 per cent of sulphur, although it at times ran as high as 60 or 70 per cent. The sulphur thus obtained contained many impurities, and it was necessary to refine it before using it as an ingredient of explosives. The refining process is described later under the subject of gunpowder. More recently, however, the sulphur used for this purpose is obtained from the residue formed in the manufacture of soda, which, until the process of reclaiming the sulphur it contained was discovered, was thrown away. This residue consists principally of calcium sulphide, and the process consists essentially of treating the sulphide with water and then subjecting it to the action of carbonic acid, which converts it into calcium carbonate and sulphydric acid. The sulphydric acid is conducted into gas-holders, where it is mixed with air, and is subsequently burned in a kiln, the products of the combustion being water (in the form of steam) and sulphur.

At ordinary temperature sulphur is a solid having a bright-yellow color, and, according to the manner in which it is prepared, may appear in the form of oblique-rhombic monoclinic crystals, or transparent rhombic octohedra. It is insoluble in water, and only slightly soluble in alcohol, benzene, and fatty oils. It is, however, quite soluble in carbon bisulphide, which property is utilized extensively in examining sulphur, and in separating it from other substances. Its specific gravity is 2.087, and under the action of heat it behaves very curiously. At 111° C. it melts; at 112° C. it appears a bright-

yellow liquid; at  $140^{\circ}$  C. it becomes dark yellow and very viscous; between  $170^{\circ}$  and  $200^{\circ}$  C. it becomes dark brown and pasty; above this temperature it liquefies again until it reaches  $440^{\circ}$  C., when it boils, evolving reddish-brown fumes. Formerly it was supposed that the principal rôle played by sulphur in explosives was that of reducing the point of ignition, due to its tendency to combine with oxygen at only a moderately elevated temperature, but the heat disengaged by sulphur during combustion makes it a far more important factor, since this property serves to greatly increase the volume of gases evolved during explosion. Although a poor conductor of electricity, when rubbed a strong electric charge is developed—a fact that must be considered in connection with making explosives containing sulphur, since neglect of it may lead to the ignition or even explosion of the mixture.

*Tests for Sulphur.*—Refined sulphur may contain as impurities earthy matter, together with traces of iron, arsenic, and antimony, while the presence of sublimed sulphur ("flowers"), even in traces, serves to develop an acid reaction.

1. Refined sulphur when finely pulverized and treated with boiling water (distilled) should show no trace of acidity when tested with litmus-paper.

2. The earthy matter present may be determined by weighing 2 gm. in a tared porcelain crucible, igniting, and placing the crucible under a bell-jar until the contents of the crucible are entirely consumed.

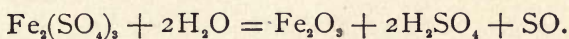
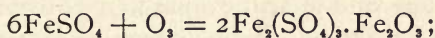
The amount of residue should not exceed 0.25 per cent.

3. The presence of iron is detected by treating the residue obtained in (2) with hydrochloric acid, and adding a few drops of potassium ferrocyanide. The minutest trace of iron will develop a decidedly blue color.

4. The presence of arsenic and antimony may be detected by means of the Marsh test, or by any of the various tests characteristic of these metals.

9. **Sulphuric Acid** (Hydric Sulphate,  $\text{H}_2\text{SO}_4$ ).—The process of making sulphuric acid was discovered about four

hundred years ago, and is still used in making the Nordhausen oil of vitriol, or fuming sulphuric acid. It consists in exposing iron protosulphate to the action of the oxygen of the air until it is converted into the basic ferric sulphate, and then drying this salt and distilling it in earthenware retorts, ferric oxide being left behind in the retorts. The reactions may be represented as follows:



The sulphuric acid thus obtained differs from that used in making explosives by its fuming upon coming into contact with the air, due to the escape of a little sulphuric anhydride, and by its greater specific gravity (1.900). The sulphuric acid used in making explosives is made as follows:

A mixture of sulphurous acid gas, air, steam, and a little vapor of nitric acid is introduced into a leaden chamber containing a layer of water. The nitric acid is reduced by the sulphurous acid gas to the state of nitrogen monoxide (NO), which takes up oxygen from the air (forming NO<sub>2</sub>) and gives it to the sulphurous acid gas, which it converts into sulphuric acid. This is absorbed by the water, forming diluted H<sub>2</sub>SO<sub>4</sub>, which is concentrated by evaporation first in leaden pans and afterwards in glass retorts and platinum stills. The properties of this acid are very characteristic. Its great weight (sp. gr. 1.842), freedom from odor, and oily appearance distinguish it from any other liquid. When absolutely pure it is perfectly colorless, but the ordinary acid has a peculiar gray color, due to traces of organic matter. It is powerfully corrosive, and when poured upon a piece of wood the latter is at once blackened. It possesses very great affinity for water, as shown by the sudden and great elevation of temperature produced on mixing H<sub>2</sub>SO<sub>4</sub> and water. This latter property is utilized in the laboratory in drying substances without the aid of heat; it is also turned to account in concentrating nitric acid, or in absorbing the water produced during a reaction in which nitric



acid plays a part, thereby keeping the latter acid up to its full strength, only the strongest and most concentrated acid being used for this purpose.

*Tests for Sulphuric Acid.*—1. The acid should be clear and colorless.

2. Determine its specific gravity as in the preceding test for  $\text{HNO}_3$ . It should not be less than 1.845 at  $15^\circ \text{C}$ .

3. Ten drops of the acid evaporated to dryness on platinum-foil should leave no residue indicative of the presence of metals.

4. Dilute 2 c.c. of the acid with 5 volumes of water. No turbidity should appear indicating the presence of lead.

5. A more characteristic test for the presence of lead is the formation of lead iodide in the form of a yellow precipitate upon the addition of potassium iodide to even dilute solutions containing lead; and the further solution of this precipitate upon adding boiling water only to separate out again in brilliant spangles upon cooling.

6. Upon diluting 2 c.c. of the acid with 10 volumes of water, acidifying with a drop of  $\text{HNO}_3$ , and adding a little  $\frac{N}{10}$   $\text{AgNO}_3$  solution, no turbidity should appear indicative of chlorine or chlorides.

7. Traces of nitric acid remaining from the process of manufacture may be determined as follows:

One part of carbolic acid (cryst.) dissolved in four parts of  $\text{H}_2\text{SO}_4$  and diluted with two parts of water, should produce no reddish-brown color, which turns yellow upon the addition of  $(\text{NH}_4)\text{HO}$ .

8. The presence of iron may be determined by diluting 2 c.c. of the acid with five volumes of water and adding a few drops of potassium ferrocyanide. The appearance of a blue color indicates traces of iron.

9. Arsenic (as well as iron) when present in sulphuric acid used with nitric acid in the process of nitration reduces the nitro-products, and should therefore not exceed more than one tenth of one per cent in amount. To detect arsenic,

dilute 1 c.c. of the acid with 10 c.c. of water, and add 2 c.c. of  $\text{CuSO}_4$ ; a piece of pure zinc introduced into a test-tube containing 5 c.c. of the mixture should not produce arseniuretted hydrogen, indicated by discoloring a strip of filter-paper moistened with  $\frac{N}{10}$  solution of  $\text{AgNO}_3$  suspended in the test-tube. (The tube should be closed with a perforated cork.)

10. The value of sulphuric acid is determined in a manner exactly similar to that used in the valuation of nitric acid, i.e., titrate with a  $\frac{N}{10}$  solution of sodium hydrate, using

methyl-orange as an indicator. Each c.c. of the  $\frac{N}{10}$  solution is equivalent to 0.0098 gm. of sulphuric acid monohydrate.

**10. Hydrocarbons.**—Although the elements carbon and hydrogen are capable of combining in almost infinite proportions, presenting various forms known as hydrocarbons, it is very difficult to cause them to combine directly. Hydrocarbons are found in nature generally combined or mixed with organic substances, from which they are separated by means of fractional distillation, and the nature of the resulting product depends largely upon the material used and the degree of heat applied to effect decomposition. Hydrocarbons containing not more than four atoms of carbon in their molecule are generally gaseous at ordinary temperature; if the molecule contains from four to twelve carbon atoms, it is a liquid, and those containing a still greater number of carbon atoms are usually solid.

All hydrocarbons may be volatilized without decomposition, possess peculiar and characteristic odors, are insoluble in water, but are soluble in alcohol, ether, carbon bisulphide, etc. Apart from the inflammable and explosive gases, only those hydrocarbons belonging to the *aromatic series* are of importance in the manufacture of explosives.

The members of this series, of which benzene may be considered the type, may be represented by the general for-

mula  $C_nH_{2n-6}$ , in which  $n$  may be any whole number not less than 6.

**Benzene** ( $C_6H_6$ ).—Benzene occurs in petroleum, but its most abundant source is the light oil obtained in the distillation of coal-tar, from which it is obtained by fractional distillation. A distinction is now recognized between benzene and *benzole*, the latter being derived from coal-naphtha, which has a lower boiling-point than petroleum or coal-tar, and is therefore the first or lighter products distilled over.

Pure benzene is a brilliant colorless liquid, exhaling a powerful odor of coal-gas; it boils at  $176^\circ$  F., and is very inflammable, burning with a smoky flame. It mixes readily with alcohol and wood-spirit, but not with water.

When subjected to the action of nitric acid, one or more atoms of hydrogen are replaced by the corresponding number of nitryl molecules ( $NO_2$ ), giving rise to various nitro-compounds, which will be considered later. Benzene is very volatile, evolving vapors which when mixed with air become explosive, and constituting a source of danger which is often overlooked.

Benzene vapor, being much heavier than air, falls to the floor upon escaping from its containing vessel, and lies there almost unnoticed, save by a slight odor which is scarcely perceptible in a laboratory, until brought into contact with a naked flame, with the result of a sudden and violent explosion. It should therefore be kept in well-stoppered bottles, and manipulated either in a hood provided with sufficient draught to carry off the vapor, or in the open air.

*Test for Benzene.*—Benzene contains very few impurities other than traces of other hydrocarbons, which do not affect its value for explosive purposes to any extent. It is, however, sometimes necessary to determine its capacity for nitration, which may be done as follows: Introduce into a fractional distilling-flask 100 parts of the benzene to be tested, and add *gradually* a mixture consisting of 150 parts of nitric acid (sp. gr. 1.42) and 200 parts of sulphuric acid (sp. gr. 1.84) which has been thoroughly cooled. This is best done



by means of a separatory funnel so as to allow the acid mixture to run in drop by drop.

During the introduction of the acid mixture the flask is cooled by immersing it in cold water. As soon as all of the acid has run into the flask, the flask is closed by a perforated cork through which a thermometer is introduced, and when the temperature becomes constant the flask is connected with a condensing apparatus, and gentle heat is applied to the flask (preferably steam heat) for about two hours. The nitro-benzene thus formed is separated from the acid by means of a separatory funnel, the last traces being removed by diluting the acid mixture with water and using the same funnel. The nitro-benzene is next thoroughly washed with water and a dilute soda solution, and finally introduced into the distilling-flask again (after having removed the water, etc.), and distilled at a temperature of about  $150^{\circ}\text{C}$ .

It is sometimes necessary to nitrate the residue a second time and redistill. Theoretically 100 parts of benzene should yield 157.6 parts of nitro-benzene.

**12. Toluene** ( $\text{C}_7\text{H}_8$ ).—Toluene, or *methyl-benzene*, is a homologue of benzene, from which it is derived by substituting for one atom of hydrogen one molecule of methyl,  $\text{CH}_3$ . It was originally obtained by distillation from balsam of Tolu, but is now prepared from tar by the same process. Toluene resembles benzene very closely in color and odor, but is slightly heavier, its specific gravity being 0.882, while that of benzene is 0.878. Another point of difference that serves to distinguish these two substances is that, whereas benzene crystallizes at  $0^{\circ}\text{C}$ ., toluene does not solidify at  $-20^{\circ}\text{C}$ . The capacity of toluene for nitration may be determined similarly as in the case of benzene.

**13. Naphthalene** ( $\text{C}_{10}\text{H}_8$ ).—Although naphthalene does not belong to the aromatic series of hydrocarbons, it is mentioned here as a substance which has been largely experimented with as a probable source for nitro-substitution explosives.

It is easily obtained in a pure state from the portions remaining at the close of distillation, by simply pressing the

semi-solid mass to remove any liquid hydrocarbons, and boiling with alcohol, from which the naphthalene crystallizes on cooling in brilliant pearly flakes, which may be still further purified by the process of sublimation.

Naphthalene smells strongly of coal-gas, is very fusible ( $80^{\circ}$  C.) and inflammable, burning with a smoky flame; it is insoluble in water, but dissolves in alcohol, ether, and benzene. It closely resembles benzene in its chemical relations, and when nitrated gives use to more numerous derivatives than benzene, all of which have been experimented with in the more modern explosives.

**14. Carbohydrates.**—This term is applied to a class of compounds containing hydrogen and oxygen in the proportion to form water, combined with six atoms, or some multiple of six atoms, of carbon. They are remarkable on account of the number of instances of isomerism they present, thus:

The formula  $C_6H_{12}O_6$  may represent ordinary *glucose* (dextrose), *grape-sugar* (lævulose), *mannitose*, or *inosite*, the latter occurring in muscular tissue, in the lungs, kidneys, etc.

$C_{12}H_{22}O_{11}$  may represent *saccharose* (common sugar), *meli-tose*, *maltose*, or *lactose* (milk-sugar).

Finally,  $C_6H_{10}O_5$  represents *starch*, *dextrine*, *gums*, *cellulose*, or glycogen, which is found exclusively in animals.

All of these substances derived from vegetable life have been used from time to time in explosives, and are still used to a limited extent, but the only one of sufficient value to merit more than passing mention is cellulose.

**15. Cellulose** ( $n(C_6H_{10}O_5)$ , perhaps  $C_{18}H_{30}O_{15}$ ).—This substance, also called *Lignin*, constitutes the fundamental material of the structure of plants: it is employed in the organization of cells and vessels of all kinds, and forms a large proportion of the solid parts of every vegetable. It must not be confounded with *ligneous* or *woody tissue*, which is in reality cellulose with other substances superadded, encrusting the walls of the original membranous cells, and imparting stiffness and inflexibility. Pure cellulose, on the other hand, has the same percentage composition as starch; but woody tissue even

when freed as much as possible from coloring matter and resin by repeated boiling with water and alcohol yields, on analysis, a result indicating an excess of hydrogen above that required to form water with the oxygen, besides traces of nitrogen. Pure cellulose is tasteless, insoluble in water and alcohol, and absolutely innutritious; it is not sensibly affected by boiling water, unless it happens to have been derived from a soft or imperfectly developed portion of the plant, in which case it is disintegrated and rendered pulpy. It is acted upon slightly by dilute acids and alkalies, but in their more concentrated forms sulphuric and nitric acids transform cellulose into other substances differing widely from the original.

Although nearly pure cellulose may be obtained from various sources, that used in explosives is generally cotton, either directly from the pods, or, since it is cheaper, the "cop-waste" from cotton-mills, or the clippings from knitting-mills. The preparation of the cotton for nitration is minutely described later.

**16. Alcohols.**—The term alcohol is now applied to a very great class of substances differing greatly in chemical and physical properties. Alcohols may be considered to be derived from hydrocarbons by substituting for one or more atoms of hydrogen an equivalent number of the univalent radical hydroxyl, OH.

They are therefore hydroxides of hydrocarbon radicals. According to the number of hydrogen atoms replaced by hydroxyl, alcohols are monatomic, diatomic, triatomic, etc.

Alcohols may also be considered as derived from the substitution for the hydrogen of the water-molecule a hydrocarbon radical of the paraffin series of equivalent atom-fixing power. When a single atom of hydrogen is thus replaced, the resulting alcohol is called monatomic, or monohydric; if two H atoms are replaced, the alcohol is diatomic or dihydric; etc.

Thus monohydric alcohols may be considered as derived by substituting the univalent radical of a hydrocarbon of the paraffin series (formed by the loss of a single atom of H) for



one half of the hydrogen contained in a single molecule of water; e.g., methyl,  $(\text{CH}_3)'$ , replacing one atom of H in  $\text{H}_2\text{O}$  to form methyl-alcohol,  $\text{CH}_3\cdot\text{HO}$ , or ethyl,  $(\text{C}_2\text{H}_5)'$ , replacing an atom of H to form ethyl-alcohol,  $\text{C}_2\text{H}_5\cdot\text{HO}$ , etc.

Similarly, when a bivalent radical of the same series formed in a similar manner replaces two atoms of H contained in a double molecule of water, the derived alcohol is dihydric; e.g., etherne,  $(\text{C}_2\text{H}_4)''$ , replacing two atoms of H in  $\text{H}_2(\text{HO})_2$  to produce ethene-alcohol, or glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$ . Finally, as an example of the trihydric alcohol, we may consider propenyl-alcohols, or glycerol, or *glycerine* derived from propane,  $\text{C}_3\text{H}_8$ , by replacing three atoms of H in a treble molecule of water,  $\text{H}_3(\text{HO})_3$ , by the trivalent radical, propenyl,  $(\text{C}_3\text{H}_7)'''$ .

*Ethyl-alcohol*.—This monohydric alcohol is the one generally referred to by the term alcohol in common acceptation, and is one of the most important substances in its application to explosives, being used either alone or in combination with other alcohols or ethers as a solvent. It is usually obtained by the fermentation of glucose, or grape-sugar, excited by yeast.

It possesses a characteristic odor and burning taste; when pure it is transparent and colorless; it freezes at  $-130^\circ.5\text{ C.}$ , boils at about  $78^\circ\text{ C.}$ , is easily inflammable, burning with a pale-blue smokeless flame. It quickly evaporates when exposed to the air, from which it also absorbs water. It mixes with water in all proportions, and, next to water, is the most valuable of all simple solvents. Its solvent power, however, depends upon its strength, which must be accurately known or determined. The strength of alcohol is estimated from its specific gravity. The specific gravity of *absolute alcohol* at  $15^\circ\text{ C.}$  is 0.794; rectified spirit has a specific gravity of 0.838 and contains 84 per cent of alcohol; proof spirit has a specific gravity of 0.92 and contains only 49 per cent of alcohol.

The following rule of thumb is given by Bloxam for calculating the approximate percentage of alcohol from its

specific gravity: If above 0.9493, multiply the difference between the specific gravity and unity by 704; if below 0.9398, subtract the specific gravity from this, multiply by 480, and add 40.

**17. Glycerine** ( $C_3H_8(OH)_3$ ).—Glycerine, or glycerol, or propenyl-alcohol, may be obtained from nearly all of the natural fats, and is also formed during the alcoholic fermentation of sugar. Glycerine is now largely prepared by the decomposition of fatty substances by means of superheated steam. Thus prepared it is obtained in great purity. It is a nearly colorless and very viscid liquid of specific gravity 1.25. When quite pure and anhydrous it crystallizes on exposure to a very low temperature, especially if agitated, as in railroad transport. The crystals are monoclinic, perfectly colorless, and melt at  $60^\circ$  F. It has an intensely sweet taste, and mixes with water in all proportions; its solution does not undergo alcoholic fermentation, but when mixed with yeast, and kept in a warm place, it is gradually converted into propionic acid. Glycerine is neutral to vegetable colors; heated, it volatilizes in part, darkens and decomposes, giving off among other products a substance called *acrolein*, ( $C_3H_4O$ ), having an intensely pungent odor.

Glycerine has a sweetish taste and is of syrupy consistency; its specific gravity at  $12^\circ$  C. is 1.269, from which it should differ but little (1.262) when used in making nitroglycerine. Pure glycerine solidifies and becomes gummy at  $-40^\circ$  C., is slightly volatile at  $100^\circ$  C., and boils at  $290^\circ$  C. It absorbs water from the air, is soluble in all proportions in water and alcohol, but is insoluble in ether.

It possesses very extensive solvent powers, which property is next in importance to its capacity for nitration, in its relation to explosives.

**TESTS FOR GLYCERINE.**—On account of the danger arising from the formation of very unstable explosives during the process of nitration of impure glycerine it is necessary to examine it carefully.

1. *For the Presence of Free Acids.*—Dilute 2 c.c. with an

equal volume of distilled water, and shake for a few minutes. Test with litmus-paper. Reaction should be neutral.

2. *For the Presence of Carbonaceous Matter.*—Put 4 or 5 drops in a watch-crystal, and heat gently. It should burn with a pale-blue flame, evolving a sweetish to pungent odor, and leave a mere trace of carbonaceous residue.

3. *For the percentage of carbonaceous matter* weigh 5 gms. in a porcelain crucible, and heat gently until it inflames. Remove the source of heat until the glycerine is consumed, and ignite the residue thoroughly (to constant weight), and weigh the remaining ash. Distilled glycerine should not yield more than 0.1 per cent of ash.

4. *For the Presence of the Higher Fatty Acids.*—Dilute as in (1), and treat with a current of  $N_2O_4$ . It should remain clear and give no flocculent precipitate.

5. *For the Presence of Butyric Acid.*—Mix 2 c.c. with 5 or 6 drops of dilute  $H_2SO_4$ . There should be no odor of sweat when the mixture is rubbed between the hands.

6. *For the Presence of Acrolein.*—Dilute as in (1), and treat with a normal solution of  $AgNO_3$ . It should give no white precipitate (which blackens on standing or boiling) within 24 hours.

7. *For the Presence of Formic Acid.*—Dilute as in (1), and treat with  $(NH_4)Ag(NO_3)_2$  (obtained by precipitating Ag from a normal solution of  $AgNO_3$  by adding  $NH_3$  and redissolving the precipitate) at ordinary temperature and in the dark. It should give no black precipitate within one half-hour.

8. *For the Presence of Glucose.*—Dilute as in (1), mix with an equal volume of KHO, and heat on water-bath. It should not become brown, and upon the addition of a few drops of  $CuSO_4$  (solution) it should give no precipitate.

9. *For the Presence of Cane-sugar.*—Mix with 5 volumes of  $H_2O$  and one half-volume of conc. HCl, and heat to  $70^\circ$  or  $80^\circ$  C. for 10 minutes. When heated with Fehling's solution for 5 minutes it should not be sensibly reduced.

10. *For the Presence of Organic Ammonias.*—Mix 3 c.c. with an equal volume of KHO in a test-tube, and introduce



into the tube above the mixture a glass rod dipped in HCl. No fumes should be given off.

11. *For the Presence of Gums and Analogous Substances.*—Mix 3 c.c. with an equal volume of a mixture of 2 parts of ether and 1 part of alcohol. The mixture should remain perfectly clear and uniform.

12. *For the Presence of Copper, Lead, etc.*—Dilute as in (1), acidulate with HCl, and treat with  $\text{SH}_2$ . It should not become discolored nor yield a precipitate.

13. *For the Presence of Iron, Zinc, etc.*—Make alkaline by the addition of  $\text{NH}_3$ , and treat with ammonium chloride and sulphydric acid. It should remain clear and colorless.

14. *For the Presence of HCl and Chlorides.*—Dilute as in (1), acidulate with  $\text{HNO}_3$ , and treat with  $\text{AgNO}_3$  (solution). It should give no precipitate.

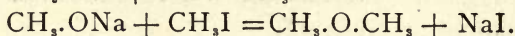
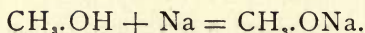
15. *For the Presence of  $\text{H}_2\text{SO}_4$  and Sulphates.*—Dilute as in (1), acidulate with HCl, and treat with  $\text{BaCl}_2$  (solution). It should give no precipitate.

16. *For the Presence of Albuminous and Coloring Matters.* Dilute with 2 volumes of  $\text{H}_2\text{O}$ , neutralize carefully with acetic acid, expel the  $\text{CO}_2$  by heat, and allow to cool. When cool treat with basic lead acetate. It should give no precipitate.

17. *For the Presence of Calcium Salts.*—Dilute as in (1), and treat with ammonium oxalate. It should give no precipitate.

18. *For the Presence of Oxalic Acid.*—Dilute as in (1), and treat with  $\text{CaCl}_2$  and sodium acetate. It should give no precipitate.

18. **Ethers.**—Ethers may be derived from the alcohols by substituting an alcohol-radical for the hydrogen of the hydroxyl group, (OH); e.g., methylic ether may be obtained by acting upon methyl-alcohol first with metallic sodium, and then decomposing sodium methyrate thus formed by means of methyl iodide. The reactions may be represented as follows, and in the final result it will be seen that the hydrogen of hydroxyl in the original alcohol has been replaced by the univalent alcohol-radical  $\text{CH}_3$ :



*Ethylic Ether* ( $\text{C}_2\text{H}_5.\text{O}.\text{C}_2\text{H}_5$ ).—This is also called sulphuric ether from its method of preparation, which consists essentially in decomposing alcohol with concentrated sulphuric acid, and subsequently rectifying the crude product. Before being used as a solvent it must be concentrated and all traces of alcohol removed.

Pure ether is a perfectly clear, colorless liquid, possessing a characteristic odor, and having a specific gravity of 0.700 at  $15^\circ \text{C}$ . It boils at  $34^\circ.9 \text{C}$ ., and evaporates rapidly in air, yielding a very heavy vapor (sp. gr. 2.59) which is exceedingly inflammable, and when mixed with air highly explosive, a property that renders it very dangerous.

It is sparingly soluble in water, but mixes with alcohol in all proportions. Its use in connection with explosives is limited to its solvent powers, since, either alone or with alcohol, acetone, or chloroform, it readily dissolves many organic substances, nitroglycerine, guncotton, nitro-benzene, etc.

The only tests necessary to be applied to ether are for its degree of concentration and adulteration; the former being determined by means of its specific gravity, and by testing for acidity, which is quickly developed by the presence of water or alcohol on account of absorption of oxygen; the latter is readily detected by evaporating a few drops upon a perfectly clean piece of platinum-foil or watch-crystal.

*Acetic Ether* ( $\text{C}_2\text{H}_5.\text{O}.\text{O}.\text{C}_2\text{H}_5$ ).—Until recently acetic ether was very extensively used as a solvent in the manufacture of smokeless powders, and its use is still retained to some extent.

It is prepared practically by distilling alcohol together with sodium acetate and concentrated sulphuric acid. Thus prepared it contains traces of acid which are eliminated by agitation with an alkaline carbonate.

Acetic ether resembles ordinary ether in appearance, but possesses a strong odor of cider; its specific gravity is 0.910;

it boils at  $77^{\circ}.5$  C., is sparingly soluble in water, and should be perfectly neutral in its reaction with litmus.

**19. Acetone.**—In its present acceptance, *acetone* refers to one particular ketone or acetone, namely, dimethyl-ketone or pyro-acetic spirit, having the composition  $\text{CH}_3\text{CO.CH}_3$ .

As a class, however, the acetones are derived from the acids by substituting for one molecule of hydroxyl, OH, of the acid group, CO.OH, another radical, usually a hydrocarbon radical of the alcohols; e.g., by substituting methyl,  $\text{CH}_3$ , for hydroxyl, OH, in acetic acid,  $\text{CH}_3\text{CO.OH}$ , we have dimethyl-ketone, or ordinary acetone,  $\text{CH}_3\text{CO.CH}_3$ . Acetone may be obtained from the distillation of wood, but commercially it is prepared by distilling the various acetates, principally the calcium acetate, which is extensively exported from this country for the purpose. The crude distillate is treated with a saturated solution of hydrosodic sulphite, again distilled with sodium carbonate, and subsequently concentrated by means of calcium chloride.

Acetone is a colorless, volatile, highly fragrant liquid, having a specific gravity of 0.81 at  $15^{\circ}$  C. and boiling at  $56^{\circ}.3$  C. It is inflammable, burning with a luminous flame, and its vapor mixed with air becomes very explosive. It mixes with water in all proportions; dissolves camphors, resins, and various organic compounds; and is one of the most extensively used solvents in making explosives, especially smokeless powders. On account of its extensive use the following tests for its purity are suggested:

*Tests for Acetone.*—1. It should be perfectly clear and colorless.

2. When mixed with an equal volume of water and thoroughly shaken, it should give no precipitate nor show any turbidity.

3. It should be perfectly neutral.

4. If traces of acidity be detected, the percentage estimated as acetic acid should not exceed 0.0025 per cent when tested as follows:

Dilute 50 c.c. of acetone with an equal volume of distilled



water; and titrate with  $\frac{N}{100}$  solution of sodium carbonate, using phenol-phthalein as an indicator (1 gm. to 1 litre of 50% alcohol). Each c.c. of the  $\frac{N}{100}$  solution is equivalent to 0.0006 gm. of acetic acid.

5. Its specific gravity at 15° C. must be at least 0.7965.

6. Distilled at a temperature between 56°.2 and 56°.4 C., 98 per cent must pass over into the receiver.

7. Tested with the weight-thermo-alcoholimeter, it should show at least 98 per cent.

8. It should contain no more than 0.1 per cent of aldehyde, which may be estimated as follows:

Prepare a solution by dissolving 3 gm.  $\text{AgNO}_3$  and 3 gm.  $\text{NaHO}$  in distilled water, adding 20 gm.  $(\text{NH}_4)\text{OH}$  (sp. gr. 0.9), and make solution up to 100 c.c.

This solution is known as the silver solution, and should be kept in a dark place.

Dissolve 10 c.c. of the acetone to be tested in 10 c.c. of distilled water, add 2 c.c. of the silver solution, and allow to stand in a dark place for fifteen minutes.

Decant from the reduced silver the supernatant liquid, and test the latter for excess of silver by adding carefully  $(\text{NH}_4)_2\text{SO}_4$  solution, which, in case of any unreduced silver being present, will produce a brownish turbidity in the liquid or throw down a brownish-black precipitate. The presence of unreduced silver indicates the presence of less than 0.1 per cent of aldehydes in the acetone.

9. The percentage of acetone estimated by the iodometric method should not be less than 98 per cent.

This method is as follows:

Dissolve 8 gm. of acetone in equal volume of water, and make the solution up to one litre. Decant 10 c.c. of this solution into a glass bottle having a capacity of not less than 250 c.c. and fitted with a ground-glass stopper. Introduce into this bottle 50 c.c. of  $\frac{N}{1}$  solution of sodium carbonate and

50 c.c. of  $\frac{N}{5}$  or  $\frac{N}{4}$  solution of iodine, close the bottle snugly, and shake for one-half hour. Next remove the stopper and introduce into the bottle 50 c.c. of  $\frac{N}{1}$  HCl, washing the stopper with the acid as it is poured in. Titrate with a  $\frac{N}{10}$  solution of sodium thiosulphate until the color produced upon the addition of clear starch paste entirely disappears. The number of c.c. of the sodium thiosulphate solution equivalent to the iodine solution must be deducted from the 50 c.c. of  $\frac{N}{4}$  or  $\frac{N}{5}$  solution of iodine previously added. 413.8 c.c. of the  $\frac{N}{4}$  solution, or 517.26 c.c. of the  $\frac{N}{5}$  solution, are equivalent to one gramme of acetone.

**20. Camphor, Vaseline, Paraffin Wax, etc.**—These substances are largely used in the manufacture of explosives, together with others too numerous to mention; but their effect is rather mechanical than chemical, and is as a rule overestimated.

*Camphor* ( $C_{10}H_{16}O$ ).—The various camphors appear to be derived from hydrocarbons by a process of oxidation, all of them being rich in carbon and hydrogen with a relatively low percentage of oxygen.

Common camphor is found in the wood of the camphor-laurel, from which it is extracted by distillation with water and purified by sublimation in vessels containing lime. It vaporizes at the ordinary temperature of the air, crystallizing in brilliant octahedra.

It fuses at  $175^{\circ} C.$ , boils at  $204^{\circ} C.$ , and is quite inflammable, burning with a thick smoky flame. Its specific gravity is 0.996; it is practically insoluble in water, but dissolves readily in alcohol and ether as well as in nitroglycerine.

Camphor is no longer used as an ingredient of smokeless powders, but enters to some extent in various dynamites,

especially those of the gelatine variety, in which it acts as a desensitizing agent.

*Vaseline, or Mineral Jelly.*—Vaseline is one of the products of the distillation of petroleum, passing over at a temperature above  $200^{\circ}\text{C.}$ , and generally consists of a mixture of two or more hydrocarbons of practically the same melting- and boiling-points. It may also be obtained from *ozokerite* (mineral wax), which is found in large quantities in Galicia, Hungary, and Russia.

Pure vaseline is a soft, yellowish, greasy substance that melts at  $32^{\circ}\text{C.}$ , flashes at about  $400^{\circ}\text{F.}$ , and at  $100^{\circ}\text{F.}$  has a specific gravity of about 0.90.

It is a very stable substance, preserves a neutral reaction under widely varying conditions, and is largely used in making smokeless powders, especially in the manufacture of the English service powder, cordite.

According to the English specifications, vaseline for use in making cordite must stand successfully the following tests:

1. It must be free from all traces of acidity.
2. It must be free from all traces of foreign (especially mineral) matter.
3. Heated for twelve hours over a water-bath ( $100^{\circ}\text{C.}$ ), it must not lose more than 0.2 per cent in weight.
4. Its specific gravity at  $100^{\circ}\text{F.}$  must not be less than 0.87.
5. Its flashing-point must be at least  $400^{\circ}\text{F.}$

*Paraffin Wax.*—Paraffin wax contains more carbon than vaseline, and appears as a crystalline solid. It is variously obtained, and, depending upon the method of its preparation, it varies in degree of hardness, melting-point, and other properties. It often develops an acid reaction, and must be melted before being incorporated in explosives. It is insoluble in water, but yields to the action of gasolene, which, however, introduces a source of danger in manipulation.

Paraffin is used quite largely in the manufacture of dynamites; but its use in smokeless powders has been practically abandoned.



Various other organic compounds, such as resins, glycerides, oils, and fats, have been experimented with in various forms too numerous to mention in a work of limited scope, their function being principally to aid in incorporating other ingredients, to moderate the action of the explosive, to act as lubricants in the bore of the guns, and for other purely hypothetical purposes.

**21. Kieselguhr, Randanite, etc.**—The first substance used to absorb nitroglycerine and thereby transform the explosive from the liquid to solid state was kieselguhr, and for an absolutely inert absorbent (or dope, as it is technically known) this material has never been excelled.

Ordinary kieselguhr consists of 63 parts of soluble silica, 18 parts of organic matter, 11 parts of sand and clay, and 8 parts of water. Its principal sources are the Lüneburg moors near Unterlüss, between Bremen and Hanover, and a recently discovered deposit of vast extent near Richmond, Virginia, U. S. A. As found naturally, kieselguhr is a soft grayish-white or reddish-white material, gritty to the touch, and readily crumbling to pieces under pressure. The organic constituent consists of the decomposed shells of myriads of diatoms, which preserve their cellular formation even after the process of calcination to which kieselguhr is subjected before being used as an absorbent for explosives. Each particle therefore acts as a reservoir for the liquid, which it retains with great pertinacity, the best varieties of kieselguhr being capable of absorbing and retaining as much as 82 per cent of nitro-glycerine.

*Randanite* consists principally of decayed feldspathic rocks, and was used as a substitute for kieselguhr by the French during the war of 1870. As an absorbent it is greatly inferior to kieselguhr in every respect.

Tripoli, coal-dust, saw-dust, various alkaline carbonates, etc., have been experimented with for the same purpose, and will be referred to subsequently.

## LECTURE IV.

### CLASSIFICATION OF EXPLOSIVE MIXTURES. EXPLOSIVE MIXTURES OF THE NITRATE CLASS.

X Explosive mixtures may be defined as the mechanical incorporation of two or more ingredients one of which must be a combustible and at least one other a supporter of combustion. Such mixtures have been divided, according to the nature of the oxidizing ingredient, into two principal classes, the *nitrate* class and the *chlorate* class.

**Explosive Mixtures of the Nitrate Class.**—In this class any nitrate may be utilized, although the majority of such chemical compounds are of but little practical value, as already indicated. On account of the force with which the oxygen is held in combination in the nitrates, it requires a powerful disturbing cause to separate it from the other elements; hence this class of explosives does not decompose very readily; their action is gradual; they are not sensitive to friction or percussion, and therefore they are comparatively safe.

The formation of the nitrates in nature has been considered very obscure, and any explanation of natural nitrification involves the consideration of many principles which are themselves but imperfectly understood.

It is now generally accepted that the natural nitrates are formed by the slow oxidation of the nitrogenous organic compounds, effected by the oxygen of the air with the aid of water and of an alkaline or earthy carbonate.

Until recently it was believed that the rôle played by the nitrates in explosives was solely that of oxidizers, and that, other things being equal, the efficiency of a nitrate depended upon the percentage of oxygen it contained. In the light of thermochemistry, we know that other and perhaps more important considerations enter the problem, and that, in addition to the amount of oxygen, the available percentage of this element, as well as the heat of formation of the salt itself, is of first importance.

Of the various nitrates experimented with, the potassium salt, or, as it is commonly known, "saltpetre," or "nitre," is, for reasons already given, best adapted for use in the manufacture of explosives.

It is the oxidizing agent used in the manufacture of gunpowder, which may be taken as the representative of this class of explosive mixtures.

**Gunpowder.**—This explosive is a very intimate mixture of potassium nitrate (nitre), sulphur, and charcoal, which do not act upon each other at the ordinary temperature, but when heated together arrange themselves into new forms, evolving a very large amount of highly heated gas. These three ingredients may be mixed in greatly varying proportions, each mixture being explosive, but there must be evidently some particular proportions which will produce the most effective powder.

Experience has shown that a powder containing

KNO <sub>3</sub> .....	75 parts
C .....	15 "
S .....	10 "
	<hr/>
	100

is mixed in the best proportions, and until recently the majority of military nations adopted it.

The percentage of the several ingredients in the service powders adopted by the principal military nations at present are given below.



## RIFLE-POWDER.

	Nitre.	Sulphur.	Charcoal.
Austro-Hungary.....	75.0	10.0	15.0
Belgium.....	75.5	12.0	12.5
China.....	75.0	10.0	15.0
England.....	75.0	10.0	15.0
France.....	75.0	10.0	15.0
Germany.....	74.0	10.0	16.0
Holland.....	70.0	14.0	16.0
Italy.....	75.0	10.0	15.0
Persia.....	75.0	12.5	12.5
Portugal.....	75.7	10.7	13.6
Russia.....	75.0	10.0	15.0
Spain.....	75.0	12.5	12.5
Sweden.....	75.0	10.0	15.0
Switzerland.....	75.0	11.0	14.0
Turkey.....	75.0	10.0	15.0
United States.....	75.0	10.0	15.0

The proportions thus adopted in service powders are not such as tend to produce the most complete combustion nor the maximum heat, but form a compromise. It is believed that better and more uniform results would be obtained from powders in which the ingredients are incorporated in proportions to produce the maximum of these two effects; an end, however, it may be said, attainable only through the application of the principles of thermochemistry.

As gunpowder is a mechanical mixture, it is necessary, in order to secure uniformity in the product, that the several ingredients should be pure, finely divided, and intimately mixed. We shall consider first the preparation of the ingredients and then the manufacture of the powder.

**Refining Saltpetre.**—Refining saltpetre is for the purpose of removing the impurities and all earthy matter which may be present, and is effected by boiling and skimming the rough or crude saltpetre in large open boilers, and afterwards drawing off the liquor and filtering it through canvas bags. The *modus operandi* is as follows: About 2 tons of saltpetre in its crude state are put into an open copper boiler capable of containing 500 gallons; about 270 gallons of water are added to this, or about .66 of water to 1 of saltpetre;

these are allowed to stand all night; in the morning a fire is lighted under the boiler, and in about two hours afterwards they will have reached a temperature of  $300^{\circ}$  Fahr. and will be boiling freely.

During ebullition by constant stirring, the light matter, containing many impurities, rises to the surface and is skimmed off (a little dissolved glue will facilitate the operation). When the scum ceases to rise, cold water is freely dashed on the surface of the boiling liquid to precipitate the chlorides that would otherwise be retained on its surface. After boiling until the solution of the nitrous salts is effected, the fire is allowed to go out; when all ebullition has ceased, the foreign salts and chlorides, being the heaviest, are precipitated. The boiler is provided with a false bottom perforated with holes, through which these impurities pass and fall to the bottom of the boiler.

In about an hour after the fire has been extinguished, the temperature of the solution falls to about  $220^{\circ}$  Fahr. A siphon is introduced, the end of which is kept about 1 inch from the false bottom of the boiler, so as not to disturb the sediment. The liquor is drawn off by the siphon into a trough, the bottom of which is fitted with four or five gun-metal taps communicating with suspended Dowlas canvas filtering-bags, of the shape of an inverted cone. If crystals form on the filtering-bags, hot water is poured over them to keep the canvas open, a constant supply for the purpose being obtained from a vessel provided with a flexible pipe, having a finely pierced rose-head, placed in close proximity to the filtering-trough. When all the liquor has passed through the filtering-bags, it is run to a cooler about 12 feet long by 6 feet wide by 1 foot deep, lined with sheet copper, and placed by the side of a washing-vat.

The liquor in the cooler is stirred by a wooden rake until the temperature is reduced to about  $180^{\circ}$  Fahr., at which temperature the mother-water separates from the saltpetre held in solution; when it falls below  $180^{\circ}$  a large number of very minute crystals are formed, which are collected and

thrown on to a wire-cloth drainer, fixed at an angle immediately above the cooler, that the strainings may run back again into the cooler; the saltpetre, when sufficiently drained, is raked into the washing-vat—also furnished with a false bottom of fine copper-wire cloth.

The whole charge receives three washings; in the first and second pure water is freely sprinkled over the saltpetre from a rose, and after standing about fifteen minutes the liquor, being very rich in mother-water and saltpetre, is run off into crystallizing-pans by a tap at the bottom of the washing-vat. In the third washing the vat is entirely filled with cold water, and the liquor, after standing for about half an hour, is drawn off; it now only contains a small quantity of saltpetre, and is not run into the crystallizing-pans, but collected in an underground tank for future use.

The saltpetre obtained by the above process is an almost perfectly pure white salt. It is placed in stone bins perforated with small holes in the ends and sides, where it is allowed to drain. The saltpetre contains from 7 to 12 per cent of water, but during the time it remains in the bins about 6 or 7 per cent is drained off. It is now fit for making gunpowder if used immediately; but if required for storage or transport it is better to evaporate the remaining water, which is done by drying in a hot chamber in the following manner:

The saltpetre is spread out about two inches thick on shallow trays of sheet copper, and placed on racks in a hot chamber heated to about  $260^{\circ}$  Fahr., by a flue under the floor. The saltpetre is stirred once or twice; from four to six hours is sufficient to evaporate the remaining moisture. It is taken out and emptied into shallow trays, allowed to cool, and then put into barrels and stored.

By the above process about three fourths of the saltpetre is crystallized, the remaining portion being held in solution by the mother-water that remains. When this has cooled to within  $7^{\circ}$  or  $8^{\circ}$  of the temperature of the atmosphere large crystals are formed, adhering to the sides and bottom of the cooler, and are collected and put with the grough into the



next charge of the boiler; the mother-liquor is collected and pumped into a boiler and evaporated to a fourth of its original quantity, and drawn off by a siphon, passed through filtering-bags, and collected in a receiver, whence it is run into copper pans of thirty-six gallons each and crystallized. The crystals obtained in this manner are pure, but contain cavities of mother-water; it is found best to use them in the next charge as grough.

Over the sediment in the bottom of the evaporating-pan hot water is poured, and the whole well stirred to extract any saltpetre that may remain; after settling, the solution is drawn off and passed through the filtering-bags previous to being run into the crystallizing-pans. Should the filtering-bags become clogged by impurities they are removed and placed in larger bags in a cleaning apparatus, where, together with the bags in which the saltpetre is imported, they are well washed in hot water; this water, containing a small percentage of nitre, is also collected in the mother-liquor tank. The bag-cleanser is also used for washing the skimmings and foreign salts, etc.; the residue with the refuse from the evaporating-pans is sold for manure.

The water from the various washings and drainings is conveyed to the underground tank, pumped into the copper boiler, and is used instead of pure water in the next charge; as it contains a small percentage of saltpetre, a less quantity of grough is required.

**Sulphur.**—Is unfit for use in a crude state; it requires to be refined. This is done by subliming and distilling.

✓ By melting, all earthy matters are left at the bottom of the retort in which the melting is done, the pure sulphur as vapor passes upward, and is sublimed and distilled by condensation at two distinct periods of its temperature. ✓

A thick, large, round cast-iron melting-pot or retort is used, built in brickwork with a furnace below. The retort has a movable lid, the joint being made air-tight by clay; the lid is sufficiently large to admit a man for cleaning out the pot. In the lid is fitted a 4-inch plug, tapered for the purpose

of charging the retort. Near the top of the retort two pipes branch at right angles, each fitted with a sluice-valve at the end nearest the retort; one of these, the subliming-pipe, from 12" to 14" in diameter, rising at an elevation of  $35^{\circ}$ , is used to conduct the vapor from the retort to the subliming-chamber situated at a distance of about 15 feet from the retort. The chamber is 12 feet in height by 10 feet in diameter at the base, dome-shaped, lined with flagstones, and the floor covered with sheet lead. Near the bottom are two doors, the inner of iron, the outer of wood, air-tight, and lined with sheet-lead. Through the bottom of these doors is a small tube leading to a cistern of water, which takes up the sulphuric acid. The outer pipe, from 7 to 8 inches in diameter and 8 feet long, is used in conveying off the vapor at a higher temperature than required for subliming; this inclines downward at an angle of  $20^{\circ}$ , delivering the vapor into a receiving-tank inclosed in an outer jacket; cold water from a cistern circulates through them, through an annular space about 1.05 inches in width. The water enters the jackets at their lowest points, and passes off at their highest, near the retort.

The receiving-tank, fitted with a movable lid somewhat similarly arranged to that of the retort, has a plugged hole in the centre, through which a rod is introduced for gauging its contents. A small pipe fitted to the top of this tank conducts any non-condensed vapor to a chamber where the "flowers" are precipitated. This chamber is occasionally cleaned out by a small door. A discharge-valve is fixed to the bottom of the receiving-tank for drawing off the sulphur into moulds.

About  $6\frac{1}{2}$  cwts. of crude sulphur are put into the retort, the sluice-valve on the subliming-pipe and the plug in the retort-lid left open, the sluice-valve on the distilling-pipe closed, and a slow fire applied under the retort; in two or three hours the raw material is melted down.

At  $170^{\circ}$  Fahr. evaporation commences, at about  $200^{\circ}$  Fahr. melting begins,  $239^{\circ}$  Fahr. the sulphur is perfectly fluid, and at 560 Fahr. it is ready for distillation. So soon as the melting begins a pale-yellow vapor arises; the plug is

inserted in the lid of the retort, the vapor passes to the dome of the subliming-chamber near the top, and falls in a shower of very fine condensed particles termed "flowers of sulphur."

After two or three hours, as the heat increases, the vapor in the retort becomes a deep reddish-brown color, when the sluice-valve on the subliming-pipe is closed and that on the pipe leading to the distilling-tank opened, the cold water constantly circulating through the jacket of this pipe and also of the receiving-tank keeps it cool, the vapor rises from the retort and passes along the pipe, becomes condensed, and runs into the tank below, a thick yellow fluid. When nearly all is distilled (which is ascertained by gauging the depth of the liquid sulphur in the tank) the sluice-valve on the distilling-pipe is shut, the fluid in the receiving-tank allowed to cool for an hour or two, when it is run off by the valve to moulds, and allowed to cool and solidify. These moulds are used wet, otherwise the sulphur will adhere on solidifying. When cool, the refined sulphur, broken into lumps, is ready for use. The vapor remaining in the retorts passes into the dome of the subliming-chamber, where it is evaporated as "flowers." The earthy matter in the retort is afterward cleaned out.

✓ The "flowers" of sulphur are unfit for making gunpowder on account of the acid they contain, crystalline or distilled sulphur only being used in making gunpowder. ✓

**Charcoal.**—Charcoal, the residue after wood has been charred, as an ingredient of gunpowder is next in importance to saltpetre. When uniformity in quality of gunpowder is required, great care must be exercised in its preparation, for the chemical composition of charcoal—i.e., the percentage carbon contained therein—will affect the quality of the gunpowder to a considerable degree; therefore extreme care has to be exercised in charring the wood. Gunpowder should contain not less than 15 per cent of charcoal.

Much depends upon the quality and condition of the wood employed. The sap should be thoroughly dried in the wood to secure the best quality of charcoal: this end is at-



tained by desiccating newly-cut timber in a hot chamber for ten or twelve days, although it is questionable if the charcoal so obtained is as good as that produced from wood that has been seasoned for a number of years. Small wood, perfectly clean, free from bark, quite dry, are essential requisites for making good charcoal.

The kind of wood commonly used is that of the willow species—the common white Dutch willow, the poplar, and the alder are generally preferred. Other woods are, however, frequently used; and for a first-class strong powder black dog-wood is said to be best, but its cost prevents its being largely adopted, except for military powders.

Distilling the wood in retorts is the method usually employed for procuring a light and equal quality of charcoal. The method of distilling in retorts is as follows: A number of retorts are set in brickwork at a suitable height from the ground floor, under which a furnace is provided; the bottoms of the retorts are protected from the direct and intense heat of the furnace by a fire-brick lining, through openings in which, and by flues, the flame passes round the retorts before reaching the chimney. The wood must be small, of eight or nine years' growth; it is obtained early in the fall, its bark entirely removed, cut into lengths of about 6 inches, and stacked for drying. When thoroughly dried it is put into a sheet-iron cylinder or "skip," having a movable lid or door at one end, which is placed horizontally on an iron carriage corresponding in height with the door of the retort; the carriage is run forward to the mouth of the retort, the cylinder containing the wood slid into the retort, which is fitted with an air-tight door, and which has previously been heated to a dull-red heat.

The process of charring commences, the steam, tar, and gas in the wood pass from the cylinder by holes in the door, through a pipe to the furnace, and are consumed. From three to four hours are required to completely char a cylinder of wood. The cylinder with its contents is drawn out of the retort by a block and tackle, lowered into an air-tight cooler

with a close-fitting lid, and allowed to remain for about half a day; it is then placed in a smaller cooler, where it remains until cold. After the charcoal has been carefully picked, it is fit for use in making gunpowder. About three charges can be burned in each retort every twelve hours.

A good and uniformly pure charcoal has, if properly made, a jet-black appearance; the fractures show a velvet-like surface, and appear the same in both large and small pieces. It should not scratch soft polished metal, and if treated with distilled water there should be no appearance of alkali.

From 20 to 25 per cent of charcoal is obtained from willow and alder, and from 25 to 30 per cent from black dogwood; the latter is very dense, tough, and of slow growth, its usual size being about one inch in thickness. When charred, it has a yellowish-looking surface, and is slightly metallic in appearance.

The kind of wood from which the charcoal has been made is known by the pith: that of dogwood is circular, and large for the size of the wood; that of the willow is also circular, but somewhat smaller; that of alder forms a figure of three equidistant radial lines.

Charcoal is very porous and quickly absorbs moisture; therefore a great store is never kept. Previous to use it is very carefully examined and picked, uncharred pieces being excluded.

To test charcoal for an alkali, finely powder a small quantity and boil it in distilled water, filter, and test with litmus-paper reddened by weak acid. Should the charcoal contain alkali, the paper will be partially or wholly restored to its color.

✓ *Pit-burned charcoal* is used in the manufacture of "pit gunpowder," and is suitable for filling fuses, port-fires, etc.; it is also used for pyrotechnic compositions and such purposes.

**Charcoal-grinding Mill.**—Before the ingredients are mixed together they must be pulverized or ground to a fine powder. Charcoal after standing a fortnight is ground in an apparatus somewhat similar to a coffee-mill on a large scale.

The mill consists of a cone secured on a vertical spindle provided with teeth running spirally over its entire outer surface; the cone revolves in a cylinder provided with teeth on its inner surface; these teeth are spiral also, but incline in the opposite direction to those on the cone.

The revolving cone is adjustable in a vertical direction to increase or diminish the space between its teeth and those of the fixed cylinder; thus a coarse or fine charcoal is produced at will. The adjustment is effected by means of two hand-wheels working on a fine screw-thread cut upon the small vertical cone spindle, which spindle can be moved upward or downward by means of the hand-wheels through the large hollow shaft upon which the bevel driving-wheel is keyed. Motion is communicated from this shaft to the small one by means of a feather upon the surface of the latter, which fits and works in a groove cut in the inside of the hollow shaft. The small hand-wheel is used for locking and securing the larger one in any required position.

The hopper above receives the charcoal. On the under side of the cone, and revolving with it, are a couple of arms that carry the ground charcoal to the discharge-spout on one side of the fixed cylinder and conduct it to a sifting-reel; this reel is simply a skeleton cylinder of wood covered with copper wire cloth having fine meshes—thirty-two to the inch.

The sifting-reel is driven by a pair of bevel-wheels set at a slight angle to allow the charcoal to run readily along the interior; as it revolves it causes the particles of charcoal to be continually rolling over each other and covering new surfaces of the reel; the fine particles pass through the meshes of the wire-cloth and fall into a receiving-bin, whilst the larger ones are thrown out at the lower end of the reel to another bin, whence they are taken and returned to the hopper. The reel and bins are inclosed entirely in a wooden framework and covering, so as to prevent the dust, which is very light, from spreading over the house. Doors are provided in this wooden covering by means of which the ground charcoal can be removed.



After being ground, the charcoal stands for about eight or ten days before using it; owing to the readiness with which it absorbs oxygen when in the pulverized state, it is apt to become heated and spontaneous combustion to ensue. The danger from this cause is much lessened when it is stored in small quantities and in separate iron cylinders or bins.

**Saltpetre and Sulphur Grinding Apparatus.**—The saltpetre, if used immediately after being purified, is so fine as to require no further reduction of its particles before mixing; but if it has been dried for storage it must, like the sulphur, be reduced to a very fine powder. They are ground separately in a small machine somewhat similar to a mortar-mill. The machine consists of a pair of edge-rollers travelling round a strong circular cast-iron bed, revolving at the same time on their own axis.

The speed of these rollers is eight revolutions per minute round the bed; they are each 4 feet in diameter, and weigh 30 cwt. Each one travels on a different path, one being near to the inside curb, or “cheese,” as it is technically called, whilst the other is farther away from the centre. A shaft or spindle common to both passes through their centres, and between them is a cross-head fixed on a vertical shaft driven by means of bevel-gearing, the pinion being secured on the main horizontal driving-shaft underneath the machine, whilst the vertical shaft, upon which the large bevel-wheel is fixed, passes through the cross-head; this latter being provided with suitable brass bushes in order to allow the rollers to rise or fall according to the thickness of the material under them.

The material to be ground, whether saltpetre or sulphur, is spread evenly over the bed of the machine to a thickness of about 1.50 or 2 inches; the rollers are then set in motion. A very short time suffices to complete the operation. The material, when ground, is shovelled from the bed into tubs and emptied into a hopper placed above a sifting-reel which is similar in all respects to the charcoal reel. As the reel revolves, certain projections provided on the shaft strike

against similar projections on the bottom of the trough that conveys the material from the hopper to the reel, and as this trough is slung under the hopper it is made to vibrate and cause the material to be shaken gradually from the hopper to the reel. The fine particles pass through a wire cloth of thirty-two meshes to the inch and fall into a bin provided; the coarse particles are thrown out at the end into another bin, whence they are taken and reground.

The ingredients are now ready for the manufacture of the powder.

**Manufacture of Gunpowder.**—The manufacture of gunpowder consists of the following processes: (1) mixing the ingredients; (2) incorporating, or “milling”; (3) breaking down the mill-cake; (4) pressing; (5) granulating, or cutting the press-cake; (6) dusting; (7) glazing; (8) second dusting; (9) stoving, or drying; (10) finishing.

*Mixing the Ingredients.*—The ingredients are carefully weighed out in the proper proportions for a 50-pound mill-charge, with an extra amount of saltpetre according to the moisture found to be contained in it; they are then placed in the mixing-machine, which consists of a cylindrical gun-metal or copper drum, with an axle passing through its centre, upon which are disposed several rows of gun-metal fork-shaped arms, called “flyers.” When in operation, the drum and “flyers” revolve in opposite directions and at different rates of speed.

After being mixed in this machine for about five minutes, the composition is passed through a hand-sieve over a hopper, falls into a bag placed below, and is tied up ready for the incorporating mill. It is now called a “green” charge.

*Incorporating or Milling.*—The incorporating-mill consists of a circular iron bed, about 7 feet in diameter, firmly fixed, upon which revolves a pair of cast-iron cylindrical edge-runners, the edges of which are now usually surface-chilled. The diameter of the runners is about 6 feet, and their width 15 inches; they have a common axle which rests in gun-metal bouches in a solid cross-head attached to a vertical shaft.

The shaft passes through a bearing in the centre of the bed, and by a system of gearing is driven by machinery which, in the latest steam-mills, is placed beneath the bed in cast-iron tanks. Each runner weighs about 4 tons, and travels with the average speed of about 8 revolutions per minute. The bed has a sloping rim on the outside called the curb, and on the inside an edge formed by the "cheese," or bearing through which the shaft passes. The runners are not equidistant from the centre of the bed, one working the part of the charge near the centre, the other the outer portion; their paths, however, overlap. Two wooden leather-shod "ploughs" attached by means of arms to the cross-head, one working next to the shaft and the other close to the curb, throw the composition under the runners.

The charge is spread evenly over the bed with a wooden rake, and contains about 2 pints of water; additional water (from 2 to 6 pints) is added from time to time, according to the state of the atmosphere. This is done for the threefold purpose of preventing powder-dust from flying about, facilitating the incorporation, and reducing the effect of an explosion in case of an accident.

During the process of incorporation a millman enters the mill occasionally, takes a wooden "shover," and pushes the outside of the charge into the middle of the path of the runners, to insure uniform incorporation of the entire charge. The action of the runners is a combination of rolling and twisting, and has, on a large scale, somewhat the effect of a pestle and mortar, crushing, rubbing, and mixing the ingredients, thereby effecting an intimate union.

The time of milling depends upon the nature of the powder. For good fine-grained powders it varies from 4 to 8 hours; the very best sporting powders require 12 hours under the runners; blasting and cannon powders are incorporated from 2 to 4 hours.

This process demands the utmost care and attention and should be conducted by experienced men, as the quality of the powder depends entirely upon this operation, and no



subsequent treatment can remedy imperfect or defective incorporation.

When the ingredients have become incorporated the product is known as "mill-cake," and it should be homogeneous in appearance, without any visible specks of sulphur or saltpetre, and of a dark grayish or brownish color, according to the charcoal used.

The mill-cake is carefully tested to ascertain whether it contains the proper amount of moisture. This should be from 2 to 3 per cent for fine-grained powders, and from 3 to 5 per cent for powders of larger granulation.

There is greater danger of an explosion during the incorporation than in any process of manufacture. The millmen only enter the mill occasionally to "liquor," or shift the charge on the bed. The building itself is made as light as possible, the roof, and front, and rear sides being constructed of very light boards, or even of canvas on wooden frames, while the partitions between each pair of rollers are of solid masonry or heavy brickwork. Directly over the bed of each mill is a flat lever-board, or "shutter," in gear with a tank of water, so arranged that when the shutter is raised on its pivot by an explosion, the water is upset into the bed; a horizontal shaft connects all the shutters in a group of mills, so that the explosion of one mill at once drowns all the remaining charges. The tanks can also be overturned by hand.

*Breaking down the Mill-cake.*—After removal from the incorporating-mill, the mill-cake is broken down, or reduced to powder-meal, so that it can be loaded into the press-box.

The breaking-down machine consists essentially of two pairs of gun-metal rollers, set in a strong frame of the same material; one roller in each pair works in sliding bearings connected with a weighted lever, so that a hard substance can pass through without any dangerous friction. An endless canvas band, with transverse leather strips attached, conveys the pieces of mill-cake from a hopper to the top of the machine, where it falls between the first pair of rollers; after passing through the second pair of rollers, which are directly

below the first, the meal falls into wooden boxes, which are placed upon carriages, and conveyed to small magazines, whence it is taken to the press.

*Pressing.*—The last operation and that of pressing the meal into a solid cake is for the purpose of fitting it to be made into a hard grain of uniform density.

The powder is brought from the small magazines to the press-house, where it is compressed into hard slabs, or sheets.

The press-box is usually of oak, with a strong gun-metal frame, and so constructed that three of the sides can turn back on hinges, or be screwed firmly together. To introduce a charge of powder-meal into the box, it is laid sidewise, the top being temporarily closed by a board, and the uppermost side alone being open, and gun-metal plates are placed vertically in the bore, being separated by narrow strips of wood, or racks, the distance between the plates being regulated by the particular kind of gunpowder required in the final product.

The meal is poured between the plates and rammed evenly, and the racks are then withdrawn.

The remaining or upper side of the box is screwed on, and the box is turned up into a vertical position, and placed on the table of the hydraulic ram directly under the fixed press-block. The pumps (which are in a separate building) are now set in motion, and the press-block allowed to enter the box. In the most improved presses, as soon as the block has reached the point to which it is desired to compress the powder, the edge of the block releases a spring and rings a bell as a signal to stop the pumps. The powder is kept under pressure for a few minutes, after which the ram is lowered, and the box removed and unloaded.

The above mode for regulating the pressure is found to give more reliable results than trusting to the indicator-gauge of the hydraulic press, for the reason that the elasticity, or resistance to pressure, of the meal varies with the amount of moisture in it, and the state of the atmosphere.

In order to secure uniform density, equal quantities of meal, containing equal amounts of moisture, must be pressed

into the same space. In practice, however, the moisture in the meal will slightly vary, whatever care be taken with the mill-cake, owing to the varying hygrometric condition of the atmosphere by the time each charge comes to the press.

It is therefore necessary to alter the exact distance the press-block is allowed to enter the box, not only with the nature of the powder, but with the season of the year, and even according to the prevailing state of the weather.

Several objects are sought in pressing the powder-meal as above described. First, the cake when made into grain of the required size absorbs less moisture from the air; secondly, the lasting qualities of the powder are greatly increased, especially if glazed; thirdly, after having been compressed, the powder is less liable to be reduced to dust in transportation. Again, by a more intimate union, or a closer juxtaposition, of the ingredients, a larger volume of gas is produced, bulk for bulk, than would result from a soft, light powder.

These qualities and others will be referred to again in a subsequent lecture.

*Granulating.* — The machine used for granulating the press-cake is somewhat similar in construction to the breaking-down machine.

It consists essentially of three or four pairs of gun-metal rollers fitted with pyramidal-shaped teeth, which are fixed obliquely one above the other in a strong framework; the sizes of the teeth vary according to the kind of grain required, but decrease regularly from the top to the bottom pair; one roller in each pair works in a sliding bearing with a counter-weight attached to prevent undue friction. Each pair of rollers is connected with that next below by a short rectangular screen of copper wire, while underneath all the rollers are placed two long wire screens fixed in a frame having a wooden bottom; both the frame and the short connecting screens are attached to the machine by strips of lancewood, and when in operation a quick vibratory motion is given to all the screens by means of a polygonal wheel upon the main frame working against a loose smooth wheel attached to the screen-



frame. The press-cake, which is contained in a large hopper, is fed to the top pair of rollers by an endless canvas band, as in the breaking-down machine, and, after passing through these rollers, it falls upon the first short screen; all that is fine enough to fall through is sifted by the vibratory motion of the screens, and travels down upon whichever screen has meshes fine enough to retain it; the pieces too large to pass through the short upper screen are carried to the next pair of rollers, and so on. At the lower end of the long screens are placed boxes to receive the different sizes of grain; the "chucks," or pieces too large for any grain, are again passed through the machine, while the dust, which falls upon the wooden bottom and is received in a separate box, goes to the mills to be worked up for forty minutes as a dust-charge.

In this machine, as in the case of the breaking-down machine, no iron or steel is exposed, and as little as possible of either metal is used in their construction, the side-frames, rollers, wheels, bolts, nuts, in short all parts except the shafts and bed-plate, being made of gun-metal, copper, or wood. The floor of the granulating-house is covered with soft leather-hide, and the shafts are encased in copper or gun-metal.

*Dusting.*—The large-grain powder, as it comes from the granulating-machine, is called "foul grain" on account of the large quantity of dust it contains, and to remove this dust the powder next passes through the dusting-reels. The reels consist of a cylindrical framework about 8 feet long and 2 feet in diameter, covered with a dusting cloth or canvas of from 18 to 56 meshes to the linear inch according to the size of the grain. The reels are either "horizontal" or "slope" according to the position in which they are fixed or the object in view.

The large-grain powders are dusted for about one half hour in a "horizontal" reel both ends of which are closed; while the fine-grain powders, containing a much greater percentage of dust, are dusted in a "slope" reel, which is open at both ends, and revolves on a shaft fixed at an angle of about

4°. The powder is poured in at the upper end of the reel, and is received in barrels placed at the lower end.

*Glazing.*—As a general rule, all large-grained powders are glazed, and recently nearly all fine-grained powders are subjected to the same process, the object being to diminish the formation of dust, and to render the powder less hygroscopic.

The glazing is generally conducted in the same building as the dusting, and the machine consists of a wooden barrel supported by and attached to a shaft running through its centre, and the whole, when in operation, revolves at about 40 revolutions per minute. The barrel is of oak, and is about 5 feet long and  $3\frac{1}{2}$  feet in diameter at the centre. The powder is introduced into the barrel through a small door, and with it about one half-ounce of graphite or plumbago to 100 pounds of powder. The door is closed and the apparatus set in motion and allowed to run for about 6 hours, at the end of which time a fine gloss will have been imparted to the grains, and all sharp angles and corners rubbed off.

*Second Dusting.*—The operation of glazing always produces a small quantity of dust, which is removed by again passing the powder through a “slope” reel.

*Stoving.*—All kinds of gunpowder are dried in the same way. The “stove” or drying-room is fitted with open framework shelves or racks, the heat being supplied by steam-pipes beneath. The powder is spread upon either copper trays or wooden frames with canvas bottoms (each having a capacity of about 12 pounds), which are then placed upon the racks. The length of time required for stoving depends upon the nature of the powder and the proportion of moisture it contains; it varies from about twelve hours for fine-grained powders to three or four days for large-grained cannon-powders; the heat ranges from 120° F. to 145° F. It is all-important that the stove should be well ventilated, so that a constant supply of hot dry air may be supplied and the air charged with vapor carried off; otherwise the moisture would be recondensed upon the powder as the temperature was lowered.

*Finishing.*—The drying process again produces a small quantity of dust, which is removed by running the powder for about three hours in a “horizontal” reel.

In addition to merely removing the dust, the finishing process imparts to the grains a very smooth, glossy appearance, even when no graphite has been used in the glazing-barrels. Large - grained cannon - powders are finished in skeleton wooden reels, and during the process a very small quantity of the purest graphite is introduced in muslin bags. Advantage is also taken of this last step in the manufacture of powder to mix together charges of different glazings, so as to secure uniform results.



## LECTURE V.

### GUNPOWDER—(*continued.*)

**Special Powders.**—For some years it has been a recognized fact that the ignition, combustion, and explosive effect of gunpowder depend in a great degree on the size, shape, and density of the grain, and that guns of different calibres require for their most efficient service powders differing in these features in order to secure the best results. The rapid increase in weight of projectiles with the increase in calibre of guns, and the comparatively smaller power of resistance of the guns, renders it necessary that the rate of combustion of the charge be regulated so as to reduce the strains on the guns as much as possible, while at the same time preserving high initial velocity to the projectile, thus rendering practicable the use of the heaviest guns, projectiles, and charges.

The amount of gas evolved at the first instant of inflammation and combustion may be measurably controlled by the size and form of the grains. Thus by diminishing the surface of ignition and increasing the density, greater resistance is offered to the penetration of the heated gases through the grains, and the rate of inflammation and combustion is correspondingly decreased.

The form of grain affecting the amount of surface exposed to combustion—that shape which offers a comparatively small surface at the first instant of ignition, increasing progressively—is theoretically the best.

Experiments by all civilized nations have settled beyond cavil the important part played by powders suited in the

above qualities to the guns in which they are to be used, and have led to the adoption of large-grain powders in heavy guns, resulting in the production, among the best, of *mammoth*, *pebble*, *cubical*, *hexagonal*, *pellet*, and *perforated prismatic powder*.

To General Rodman, Ordnance Department, United States Army, belongs the honor of the first investigation and practical results which led to the introduction of the so-called "*progressive powders*." Without changing the composition of the powder, General Rodman clearly demonstrated by his experiments with the 15-inch and 20-inch cast-iron guns that the initial pressures developed by the large charges of powder necessary for the service of guns of large calibre could be controlled by merely compressing the fine-grained powder previously used so as to form larger grains of greater density. The first compressed powder was the Rodman *mammoth* powder, some of the grains of which were three inches in diameter. This powder was quickly imitated in the *pebble* powder, which differed only in the size of grain, the granules varying in size from one-half inch to one inch, the density being about the same as that of the *mammoth* variety, 1.80.

The principle upon which the compressed powders were made is as follows: In a large charge of fine-grain powder, a relatively very large surface of inflammation is presented at the first instant of ignition, and the greater part of the charge is burned with the production of a great volume of gas before the projectile has moved far from its original position in the bore of the gun, and while the powder-chamber is at its minimum, the result being the development of the maximum pressure at the base of the bore, which rapidly diminishes as the projectile moves down the bore, thereby allowing the gases to expand.

The average force developed by the combustion of such powders is small compared with that exerted at the first instant of explosion.

The object of progressive powders is to reverse this order by presenting the smallest surface of inflammation at the begin-

ning so as to develop only sufficient gas to overcome the inertia of the projectile, and to have the quantity of gas increase regularly as the projectile moves down the bore so as to distribute the pressure throughout the gun and avoid the intense local action developed by the older powders.

In the compressed powders it was sought to attain this result by the combustion of the successive layers.

Thus in the "Fossano," or "Progressive Powder," used in the 100-ton gun at Spezia, the press-cake was broken up into grains varying in size from  $\frac{1}{8}$  to  $\frac{1}{4}$  of an inch in diameter, mixed with a certain percentage of rifle or mortar powder, and then subjected to a second pressing. The density of the first press-cake was about 1.79, which was reduced by the second pressing to a mean density of about 1.76. The second press-cake was subsequently regranulated, each grain being about  $2\frac{1}{2}$  inches in length and breadth by about  $1\frac{3}{4}$  inches in thickness, and consisting of a mixture of powders having two separate specific gravities, or densities.

These investigations soon led to the adoption by military nations of some regular form of grain for powders instead of the irregular shapes of the original mammoth and pebble powders.

Other modifications having the same general object in view were introduced from time to time, and serve to distinguish the various special powders now in use.

**Hexagonal Powder.**—The hexagonal powder used in guns of large calibre in the U. S. Army is manufactured by Messrs. E. I. Dupont & Co. The uniform size of grain and their polyhedral shape insure great uniformity in position and size of the interstices in the cartridge; this insures, with a uniform density of grains, uniformity in density of loading, the result being equal and low pressures, together with uniform and good velocities.

**Manufacture of Hexagonal Powder.**—The proportions of the ingredients of hexagonal powder conform to the United States standard, and up to the completion of the incorpora-



tion in the wheel mill, its manufacture is like that of ordinary powder.

*Mealing*.—The mill-cake is revolved in a cylinder of wire-woven cloth, with *wooden* balls, until it is *mealed*.

*Pressing*.—The mealed powder is then carefully pressed between horizontal metallic plates or dies. The powder comes out in a sheet or cake of polyhedral granules united along their edges, the dies being nearly perfect dodecahedrons.

*Graining*.—The press-cake is passed between rollers armed with brass cutting teeth at an angle of from  $60^{\circ}$  to  $120^{\circ}$  to the axis, which cut the cake into granules, their cross-section being almost *hexagonal*, whence the powder derives its name.

*Glazing*.—The powder is then sent to the glazing-mill and glazed.

*Brushing*.—The powder is next passed repeatedly through the brushing-machine. This consists of a frame with brushes revolving near an inclined plane along which the powder passes by the motion of the brushes.

*Drying*.—The brushing ended, the powder goes to the drying-house, where it is dried. The powder is now minutely examined, its specific gravity taken, and a count made of the granulation; a variation of two granules to the pound being enough to condemn the powder.

*Rebrushing and Redrying*.—If satisfactory, the powder is again passed through the brushing-machine, redried, and then receives a third brushing.

*Packing*.—The powder is now packed in barrels and is ready for inspection.

**Perforated Prismatic Powder.**—The adoption of this form of powder by some nations, and production of suitable machinery for its manufacture, necessitated the use of presses of peculiar construction to insure sufficient and uniform density: the press to be so devised as to produce uniform size and shape of grains, and allow their ready withdrawal from the moulds; the surfaces such as to allow close packing in a given space. These considerations led to the adoption of a regular geometrical figure; the hexagon offers a good shape

for piling, the angles being all sufficiently obtuse to prevent breaking or spawling at the edges. Each layer and the whole cartridge is easily made up. Perforations were found necessary to insure better and more uniform control of combustion in the grain. The number of perforations first adopted was seven—one central, the other six at equal distances from the central one,—although one perforation in the centre has been found sufficient.

The ingredients for the manufacture of the powder-base are the same as used in manufacture of ordinary powder. The pulverized materials for 220 pounds are placed in a wooden drum lined with sole-leather, with 330 pounds of bronze balls, and subjected to 1440 revolutions at the rate of 8 or 10 per minute. The powder is then brought to the moistening-table of wood surrounded by an upright edge, over which is suspended a graduated glass measure having a copper pipe and rose at the bottom. On the table a charge of 55 pounds of powder is spread and moistened with  $2\frac{3}{4}$  quarts of distilled water. It is then passed from a hopper to an endless canvas belt 20 inches wide, between a lower paper and upper bronze roller weighing 2425 pounds, making a revolution in twelve minutes. The bronze roller can be weighted to exert a pressure of 60,000 pounds. The powder is then broken into coarse lumps by wooden mallets and granulated to two sizes of grains: the first, cannon-powder—used for manufacture of the prisms—is passed through a sieve of 0.26 inch diameter of holes.

**Manufacture of Perforated Prismatic Powder.**—Ordinary grain powder, made as above, is of a specific gravity of 1.5, and too elastic for use in the press. By reworking it loses a part of its elasticity, and is then fit for formation of the prisms by the following process: The powder-base, as above, is moistened with 10 per cent of water, passed through the spindle-press with the prescribed pressure, and granulated, the grain and dust being collected in a receptacle. This mixture of grain and dust is dried in the air or by artificial heat till  $1\frac{1}{2}$  per cent of the moisture remains. It is placed in a mix-

ing-drum—220 pounds of powder and 330 pounds of bronze balls—and subjected to 1440 revolutions, moistened and pressed as before, giving it a specific gravity of 1.675 to 1.75. It is granulated and separated, the cannon size again dried by air till 6 per cent of moisture in dry weather remains, and placed in barrels covered with damp cloths for use.

The press for this purpose is constructed to give a pressure of 65,000 pounds per square inch. It consists of a heavy casting on a stone foundation, a main and secondary shaft, one fixed and two movable cross-heads. These have each six hexagonal stamps perforated with seven holes, which enter corresponding hexagonal moulds on the lower cross-head. Six groups of seven needles are fixed in such position that they extend up through the perforations of the lower stamps throughout into the moulds and enter the perforations of the upper stamps as the latter descend to press the powder in the moulds; these form the perforations in the prisms. Eccentrics and cranks operating the cross-heads are timed so that when the upper stamps have reached the lowest point of descent the lower ones are moving upward, giving the extreme pressure, after which the upper stamps ascend and the lower ones simultaneously push the perforated prisms up from the moulds. The lower stamps constitute the bottom of the moulds. The moulds are filled from a hopper having a table with forward-and-back motion, containing six suitable measures which receive the powder from the hopper; the charging-table moves forward and drops the charge in the moulds; its edge carries the prisms brought up from the mould to an inclined shelf, whence they are removed. The capacity of the powder measures can be regulated as desired. Two rooms are required for each press—one for the press, the other for the prisms.

Before starting the press, the mould-needles and stamps and all rubbing-surfaces ought to be oiled with a light, pure oil or graphite.

All surplus lubricant must be wiped off. The powder to be pressed ought to have at least  $5\frac{1}{4}$  per cent of moisture. The moist prisms weigh about 620 grains each, and must not



vary more than 5 grains. The first two sets of prisms should be rejected because of excess of oil. Three men can work a press; a carrier for every press is also required. The height and weight of the prisms are verified from time to time, and the powder in the hopper is stirred from time to time. Loose powder is brushed away from the stamps and top of the moulds; and all rubbing-surfaces are lubricated as often as once an hour. If a needle breaks, the press is stopped and the needle replaced. On dry days the powder loses moisture; this is indicated by increased height of prisms or vibrations of the press, in which case it is moistened with  $\frac{1}{4}$  per cent of moisture, which is done in a drum by a fine rose-sprinkler. The prisms pressed by the press contain about 5 per cent of moisture, and must be dried to about  $\frac{3}{4}$  per cent by exposure to air or on shelves in a suitably arranged drying-room; they are then exposed to a temperature of 120° Fahr. for 48 hours, and are ready for packing.

The prisms are packed in wooden boxes in layers (12 rows of 14, and 11 rows of 9, 6 deep) weighing about 110 pounds to the box.

The prisms are regular hexagons 0''.992 high and 1''.6 width across the angles. The packing-boxes are of inch stuff, and may be tin-lined. Two sheets of felt—the smaller at one end, the other on top—keep the prisms from rubbing against each other in transportation.

The boxes have rope handles, and are marked with the weight, kind, place, and date of fabrication of the powder.

**Pellet Powder.**—Pellets are formed by compressing the powder meal into metal moulds. Various shapes and sizes were tried: some were flat disks, others prisms; but the shape which found much favor at first was the cylindrical pellet  $\frac{3}{4}$  inch in diameter by  $\frac{1}{2}$  inch in length, and weighing 9.5 grains. Originally these were made by hand, but it was soon apparent that, if required in large quantities, machinery would have to be devised for their production; consequently a large machine, of somewhat novel description, and capable of making 400

pellets at one time, was designed by Dr. John Anderson, and manufactured in Birmingham.

**Manufacture of Pellet Powder.**—This machine is worked entirely by means of hydraulic power derived from an accumulator, which affords a pressure equal to 1000 pounds per square inch. The machine consists of two hydraulic cylinders, with a division in the centre of each, thus in reality making four cylinders; in the two upper ones a plain cylindrical ram is fitted, which merely rises and falls as the water is admitted underneath the ram or is withdrawn. These rams are used, first, for compressing the pellets, and second, for ejecting them, when finished, out of the mould-plates. The two lower divisions are fitted with piston-rams, securely attached to cross-heads which are united together, and also connected to two other cross-heads above the cylinders by means of strong wrought-iron side rods, provided with collars working between lugs cast upon the hydraulic presses, and so adjusted as to allow only a certain limited travel either up or down. The upper cross-heads can be adjusted to their exact positions by means of screw-threads and lock-nuts on the upper end of the side rods. The use of the lower piston-rams is to close the upper openings in the mould-plates by bringing the top punches, which are connected to the upper cross-heads by a gun-metal plate, down upon the mould-plate, and thus confine the powder meal in the moulds. The upper rams are now slowly raised, and these, acting upon the lower punches, compress the powder in the mould plate. After the proper density has been secured, the action of the lower rams is reversed, by which means both the lower and upper cross-heads receive an upward motion, thereby raising the upper punches clear out of the way, so as to admit of the compressed pellets-being ejected out of the mould-plate, and this is done by giving a further upward motion to the two plain cylindrical rams.

To compress the powder in the mould and form a pellet requires four distinct movements of the machine. First, the upper punch is brought down until it rests upon the mould-

plate and closes the mould; this is effected by a downward motion of the two lower piston-rams, to which the upper and lower cross-heads are connected together with the upper punches. Secondly, the lower punches are raised by the two upper plain rams, and the powder is compressed in the mould between the two punches. Thirdly, when the pellet is sufficiently compressed the upper punches are raised from the mould-plate, this being done by reversing the action of the two lower piston-rams until the upper cross-head and punches are at a sufficient height to admit of the compressed pellet being ejected out of the mould-plate. This fourth and last operation of ejecting the pellet is effected by allowing the upper plain rams to rise still further, and thus force the finished pellet out of the mould by means of the lower steel punches.

It is seen that a machine of this description is capable of making pellets of almost any shape, such as cylindrical, hexagonal, prismatic, or—what is possibly the best of all—spherical, by merely altering the form of the mould and punches. In the machine referred to there are (on a revolving table, the framework of which is made of gun-metal) four mould-plates fitted; each contains 200 holes, but as there are only two hydraulic presses to the machine it follows that only two sets, or 400 moulds, are under compression at one time; so that if we number these mould-plates consecutively, then Nos. 1 and 3 will be under pressure whilst Nos. 2 and 4 are being filled. When the powder in Nos. 1 and 3 mould-plate is sufficiently compressed, and the pellets formed therein have been removed, the entire table is turned one fourth of the way round by means of a handle and a toothed pinion working into corresponding teeth provided round the periphery of the gun-metal table. Nos. 2 and 4 mould-plates, which have been wholly filled with meal-powder, are now brought under the cross-heads of the machine and are in position for the powder contained therein to be compressed into pellets, whilst Nos. 1 and 3 in turn take their places to be refilled; the operation, therefore, of pressing and refilling are continuous,



and the machine is capable of producing a large quantity of pebble-powder per day, and with very little waste.

**Cubical Powder.**—Since the pellet-powder was first brought into use, another description of large-grain powder, called “pebble-powder,” has been introduced for service with guns of large calibre. The pebble-powder is formed of large grains ranging from eleven sixteenths of an inch to as much as 2-inch cubes; to manufacture this class of powder expeditiously and cheaply has brought forth another description of machine for forming the pebbles by cutting up previously compressed cakes into cubes of the required dimensions. This is done in the following manner:

**Manufacture of Cubical Powder.**—The cake as brought from the press-house is of the thickness of the required cubes; this cake the machine has to cut up—first, into long strips of the same width as the thickness of the cake; and, secondly, to cut these long strips transversely into cubes. This is accomplished in the machine by means of two pairs of rollers in the following manner: The cake is fed to a hopper immediately above the first pair of rollers, provided with knives upon their surfaces to cut the cake into long strips. The strips fall on an endless travelling band, which conveys and carries them to the second pair of rollers, where they are cut transversely into cubes. Then they drop into a spout, and are delivered to a revolving sifter covered with copper wire, which conveys the cubes to a number of wooden boxes contained in a small gun-metal truck; the dust and small pieces fall through the sifter into other boxes, and are taken back to the press-house and worked up again.

**Modifications in the Manufacture of Gunpowder.**—Several processes of manufacture have been suggested as substitutes for the old and rather slow method just described, and many have been experimented with, but except in cases of great emergency, when quantity rather than quality is demanded, the old methods have been retained so far as to include the preparation of the press-cake.

In the case, however, of powders of regular granulation,

and compressed powders generally, the rapid advances made in mechanical devices and labor-saving machines have greatly increased the output of modern powders over that of the older form of granulation, which is at present limited almost entirely to rifle or small-arm and blasting powders.

**Process followed at the Augusta, Ga., Mills.**—In 1862 or 1863 Col. G. W. Rains introduced into the Confederate Powder-mills, Augusta, Ga., a process of mixing which was claimed to be so much more thorough that the time required for incorporation was reduced three fourths.

The sulphur and charcoal were severally pulverized and bolted; the nitre (pulverized by disturbed crystallization) was added to these, and the mass, roughly mixed, was moistened with water and introduced into horizontal cylinders of sheet copper, 30 inches long by 18 inches in diameter. These cylinders revolved closely on a common axis consisting of a heavy brass tube 3 inches in diameter, perforated within the cylinders by a number of holes one-eighth inch in diameter. High pressure was introduced through this tube, raising the temperature to the boiling-point, while the water produced by condensation, added to that originally used to moisten the materials, reduced them to a semi-liquid slush, which was run out of the cylinders after about eight minutes' rotation. On cooling, this mud became a damp, solid cake, the nitre, which in the state of boiling-hot saturated solution had entered into the minutest pores of the charcoal, now recrystallizing. The cake so produced was transferred to the incorporating mills, and under 5-ton rollers was in an hour brought to the condition of finished mill-cake, ready to be cooled and granulated, while without the steaming process four hours' incorporation in the mills had previously been necessary to produce powder of the same first-class character. The capacity for work of the mills was thus practically quadrupled, the thorough saturation of the charcoal with nitre being accomplished by the steaming, while it remained for the rollers merely to complete the mixture of the whole mass and give the required density to the mill-cake.



**Wiener Process.**— This powder, invented by Colonel Wiener of the Russian Artillery, differs in its manufacture from the ordinary powder in that all of the moisture is eliminated in the press-mill, the mixture here being brought to a temperature of  $240^{\circ}$  F., the melting-point of sulphur. In this manner equal densities were obtained, but the resulting grains were very porous, and consequently had a great capacity for moisture.

**Nordenfelt and Meurling Process.**— This process was devised in order to reduce the danger attendant upon the manufacture of powder. The carbonaceous matter is first ground to a very fine powder, and then the sulphur is prepared for use by dissolving it in carbon bisulphide. The solution is effected by the aid of a gentle heat in a warm bath, and the evaporation of the bisulphide is prevented by covering it with a layer of water.

A saturated or nearly saturated solution is thus prepared. The pulverized carbonaceous matter and the solution of sulphur in  $CS_2$  are then thoroughly mixed together in a closed vessel containing a mechanical stirrer. When the mixture is complete the solution is evaporated or distilled off by the aid of a gentle heat. According to the inventors, when the  $CS_2$  is evaporated the carbonaceous matter and sulphur remain intimately mixed, and each particle of carbonaceous matter is impregnated with sulphur, instead of at present, where the admixture is obtained by grinding, the particles C and S being mechanically placed side by side. The saltpetre is prepared for use by dissolving it in water; the solution is added to the pulverized carbonaceous matter already impregnated with sulphur as described, and the whole is stirred together in a mechanical mixer.

**Modifications in the Composition of Gunpowder.**— Besides the changes in the methods of manufacture, there have been several changes proposed in the chemical composition, in the physical condition, and in both chemical composition and physical condition of powders.

The most notable change in the composition of modern



gunpowders is shown in the so-called "Brown Prismatic" or "Cocoa Powder," which was introduced into Germany in 1882.

*Brown Prismatic or Cocoa Powder.*—The exact nature of this powder, both as to the ingredients themselves and their proportions, was for some time shrouded in mystery, the name "Cocoa" tending to this end, as it was evidently intended it should. There is now no doubt that the peculiar brown color of this powder is due to the charcoal, which, as already stated, is prepared by carbonizing rye straw.

In 1884, Professor Munroe, at that time Professor of Chemistry at the U. S. Naval Academy, analyzed a sample of this powder made at the Rottweil-Hamburg Powder Works at Duneberg, and marked c/82, with the following result:

"The powder was in the form of perforated hexagonal prisms, color of cocoa, of a hardness of between 2 and 3 on Mohr's scale, and a density reported as 1.86 grams. Qualitative analysis showed the presence of potassium nitrate, sulphur, charcoal, and water. The charcoal was of a reddish color, and behaved towards alkaline hydroxides like underburnt charcoal. The action was specially marked with ammonium hydroxide, as it dissolved out a marked quantity of humus-like substance, Water also yielded a marked amount of infusion.

"Quantitative analysis gave:

	I	II	III	IV	Mean.
Moisture.....	1.05	1.10			1.08
Nitre.....	80.52	80.36			80.44
Charcoal.....	15.80	15.99			15.90
Sulphur.....	2.19	2.26	2.24	2.28	2.24
					<hr/> 99.66

"The charcoal contained:

	I	II	III	Mean.
Carbon .....	48.43	48.17	48.39	48.33
Hydrogen.....	5.58	5.60	5.53	5.57
Oxygen.....	44.64	44.93	44.75	44.77
Ash .....	1.35	1.30	1.33	1.33
				<hr/> 100.00

“ It is to be seen by these analyses that the cocoa powder differs markedly from the U. S. regulation powder—

“ 1st. In the proportions of the ingredients:

U. S. Regulation Powder.	
Nitre.....	75.00
Charcoal .....	15.00
Sulphur.....	10.00
	<hr/>
	100.00

“ 2d. In the character of the charcoal, which is red instead of black.

“ In order to learn more of the nature of the charcoal, a partial analysis of the ash was made. The ash was red-colored. It yielded:

Silica.....	13.93
Ferric oxide.....	25.40
Alumina.....	8.32
Lime.....	28.50
Magnesia .....	7.28
Undetermined.....	16.57
	<hr/>
	100.00

“ The presence of alumina in the ash seems to point to the club-moss or some similar lycopodiaceous plant as the source of the charcoal.”

**Properties Peculiar to Cocoa Powder.**—One noteworthy peculiarity of cocoa powder is its velocity of combustion, which is so low that a grain may be held in the hand and ignited, and then placed on the ground before the burning portion reaches the fingers.

With a single grain weighing 42.4384 grams, the time of burning was 17 seconds. Even when powdered it burns much more slowly than pulverized *black* powder, which would show that the slow combustion was not due to the great density and hardness only.

The advantage of the cocoa over other powders exists in its

property of imparting a high initial velocity to the projectile, while exerting a relatively low pressure on the walls of the gun. This is due to a number of causes, viz.:

1. The form of the grain.
2. The size of the grain.
3. The great density of the grain.
4. The great hardness of the grain.
5. The small percentage of sulphur.
6. The easy inflammability of the charcoal or carbohydrates.
7. The relatively great heat evolved.
8. The simplicity of the chemical reaction as shown by Noble.

(5) tends to reduce the readiness with which the powder will ignite or raises its point of ignition, even when the grain is pulverized.

(1), (2), (3), (4), and (5), combined, operate so long as the first four exist to produce a very slow rate of combustion. By the time, however, that the projectile is moved from its seat, the grains will be reduced in size and more or less broken up. We then have a finer-grained powder, which is highly inflammable at the temperature which exists, and consequently the volume of gas evolved will increase rapidly as the volume of the chamber increases. Owing to the relatively great amount of heat evolved (7), the cooling effect of the envelope is less marked than with other powders. From the comparatively simple chemical reaction it is probable that the rapidity of the reaction is more uniform than in the more complex reactions resulting from the explosion of other powders.

**DuPont Brown Powder.**—In 1887 the DuPont Company produced a brown powder which equalled, if it did not excel, the powders of the same class previously used abroad. In his specifications Mr. Eugene DuPont sets forth the nature of the new powder substantially as follows:

To obtain a powder possessing great ballistic power, and at the same time obviate, partially at least, the disadvantages arising from the combustion of the powder due to the great



volume of smoke, the ordinary charcoal previously used in the manufacture of gunpowder is replaced by a grade of charcoal specially prepared so as to change the relative proportions of the carbon, hydrogen, and oxygen, and also so that the burnt wood shall retain its fibrous nature.

To this charcoal is also added substances termed "carbohydrates," in which the elements hydrogen and oxygen occur in the proportions to form water, which is also one of the objects in preparing the charcoal used, the other object being to have the carbon in its cellular state, which it retains even after having been ground very fine, so as to more readily combine with the oxygen liberated from the nitre upon explosion of the charge. The greater proportion of the oxygen and hydrogen in this charcoal, and the addition of the carbohydrates, have the following effect upon the action of the powder:

The temperature after ignition of the charge in the gun is approximately 4000° F.—a degree of heat too high to permit hydrogen and oxygen to unite to form water. These elements therefore remain dissociated until the gases expand, due to the projectile moving down the bore of the gun. This expansion is accompanied by a fall of temperature, which continues until a point is reached at which the hydrogen and oxygen do combine chemically and form water. This chemical combination is in turn accompanied by evolution of heat, which serves to convert the water from a liquid into a gaseous state, which, together with the other gases formed during the combustion of the powder, is again expanded, and exerts an additional pressure upon the projectile. The pressure is thus gradually developed and uniformly sustained while the projectile is in the gun, thereby insuring much higher velocities than were possible under the old conditions.

Moreover, the steam thus generated, which adds its expansive force to that of the other gases, aids in dissipating the smoke consequent upon explosion by becoming condensed as soon as it reaches the air, and, in the form of water, absorbing a large portion of potassium carbonate, which forms a large proportion of the solid residue of the result of decom-

position of the powder and that portion which appears as smoke.

The same factors that tend to establish the superiority of the Rottweil-Hamburg powder obtain equally in the brown powder made in the United States; while the addition of the carbohydrate and the mode of preparing the charcoal also serve to improve the latter powder. According to Berthelot, the combustion of the hydrocarbons yields more heat than that corresponding to the carbon they contain, the hydrogen and oxygen being supposed in the state of pre-existing water, that is to say, no longer contributing to the production of heat. The heat of combustion of a carbohydrate of the formula  $C_6H_pO_p$  is, according to experiment (Berthelot), generally from 709 cal. to 726 cal. for 72 gm. of carbon.

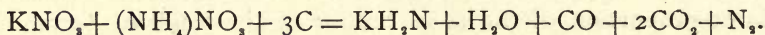
When the carbohydrates are dehydrated by heat, a portion of this excess of heat remains in the residual carbon, which also sometimes retains an excess of hydrogen capable of yielding, weight for weight, four times as much heat as carbon.

These facts, considered in connection with the important rôle played by dissociation, indicate other reasons for the superiority of these new powders.

**Amide Powder.**—F. Gaens has proposed and patented the use of a gunpowder differing from the old gunpowder still more radically in composition than brown powder does. It consists of—

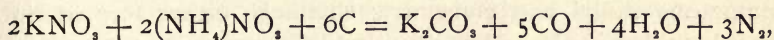
Potassium nitrate .....	101 parts.
Ammonium nitrate .....	80 “
Charcoal .....	40 “

The theory is that when these components are employed in suitable proportions, *potassamide*,  $KH_2N$ , is formed on ignition of the powder, that the *potassamide* is volatile at high temperatures, and increases the useful effect of the powder. The reaction is represented as follows:



The patentee claims for this powder that when burned it leaves very little (if any) residue, produces no gases injurious to the gun, and much less smoke than ordinary gunpowder does. This proposal is very interesting, and the advantages claimed for the powder are most important; but there is no statement in chemical literature of the existence of a potassamide volatile as such.

The explosive reaction, resulting from such a mixture would probably be represented as follows:



the products being those resulting from the explosion of ordinary gunpowder, the ammonia being oxidized into water and nitrogen; there would also be some interreaction between carbonic oxide and water-vapor at high temperature, with the formation of some  $\text{CO}_2$  and  $\text{H}_2$ . The volume of total gases produced by the ignition of such a powder would be very large, and its rate of burning would be likely to be slow (from the absence of S).

Krupp's report of October, 1888, contains an account of trials of new kinds of powder furnished by the United Rhenish-Westphalian powder factories. These were of two kinds, a large-grain and a prismatic powder; their composition is not given, but from the properties attributed to them of giving but little residue, thin smoke, and of being highly hygroscopic, it is very probable that they contain  $(\text{NH}_4)\text{NO}_3$ , and are similar to Gaen's Amide Powder. The grain powder, suited for use in guns of small calibre, was tried in guns of 4- to 8.7-centimetre calibre (1".58 to 3".42), and found to give considerably less pressure in the powder-chamber for equal velocity than the German service grain and cubical powders which were tried in comparison, the new powder being stated to be about  $1\frac{1}{4}$  to  $1\frac{1}{3}$  times as efficient as the old.

The prismatic powder suited for medium-sized guns was proved in 10.5- and 15-centimetre guns (4".13 and 5".9), with the result that the new powder was found to be more efficient per unit of weight than the *brown prismatic powder*, giving



less pressure for the same velocity; and it was stated that, without exceeding a safe limit of pressure, the new powder could give velocities which could not be reached by the brown prismatic powder.

**Quick Powder.**—Mr. G. Quick has taken out several patents for improvements in cartridges for ordnance. The first (1884) is for the pressing of disks or cakes of gunpowder (or other gas-producing explosive) with a large central cylindrical hole and smaller radial one, which are connected by numerous radial and concentric channels, either formed on the flat sides of the cakes by suitable means in the pressing, or subsequently cut or drilled in them. The object of these channels is stated to be for the spread of the flame equally and rapidly in all directions, over and between the surfaces of the cakes as well as through the perforations in them, so that the whole cake and the whole of the charge may be ignited with great rapidity and burnt with great uniformity. The objects, it may be noted, differ from those aimed at in the Rodman perforated cake. The central hole should bear some relation to the proposed diameter and the length of the cartridge; the disks may be of any required thickness, from one-half inch, to six or more inches, and any number may be employed to form a cartridge or charge, the central holes being kept in the centre of the cartridge, and the other holes corresponding to each other.

The disks may be of the same diameter as the powder-chamber of the gun, or they may be smaller, and the annular space may be filled with any other description of powder.

One of the specifications claims the use of the solution of guncotton, or of celluloid or similar material, as a cement or water-proof coating for the individual cakes forming a cartridge; and in the 1888 specification, instead of disks, he proposes the compressing of gunpowder or other explosives in the form of segments of a circle (they appear from the drawing to be sectors of a circle), so that when placed together they form rings or disks of a diameter suitable to the powder-chamber of the gun. The segments are provided with pro-

jections and recesses to lock the segments of the cakes and the individual cakes one to another, so as to prevent any twisting or sliding movement; the junctions of the segments being so disposed that the segments "break joint" with respect one to another, the whole thus forming a rigid cylindrical cartridge or charge.

**Noble's Powder.**—In 1886, Colonel W. H. Noble proposed to build up cylindrical charges for guns, practically in the same manner patented by Mr. Quick two years later. Colonel Noble also claims improvements in the preparation of charcoal for gunpowder, with a view of obtaining charcoal of uniform chemical composition. In charring wood, he proposes to previously crush it, to char some of it rapidly and some slowly, so as to produce charcoals containing different percentages of carbon, to be ascertained by analysis, and to make a blend of the charcoals in such proportion as to furnish a charcoal containing the desired amount of carbon. He also proposes to employ uncharred turf or bogstuff (previously washed, dried, and ground) either alone or mixed with charcoal.

The subject of smokeless powders (except those having ammonium nitrate for the base), at least such as have as yet appeared, belongs properly to the class of explosive compounds, and will be considered subsequently.

**Saxifragine.**—In this powder, barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , is substituted for nitre with the view of producing a slower-burning gunpowder, the proportions of the several ingredients being as follows:

Barium nitrate .....	77.00 parts
Charcoal .....	21.00 "
Sulphur .....	2.00 "

The barium nitrate used is prepared by treating the chlorate with sodium nitrate, and the process of manufacture is identical with that of gunpowder. The inflammability of the powder is increased by dusting the grains of the finished product with meal-powder. Experiments with this powder

have proved it to be unfit for a propelling agent, its rate of combustion being too slow for use in small-arms, and the property of greatly fouling the bore precluding its use in guns of heavy calibre.

The only advantage claimed for this class of powders was its low rate of combustion, an end that can now be accomplished at will by varying the physical characteristics of ordinary gunpowder, and it has therefore almost entirely disappeared.

**Blasting-powders.**—Although, on account of its hygroscopicity, sodium nitrate cannot be used in the manufacture of military gunpowders which are generally made in large quantities to be stored for years, this substance appears as the principal ingredient in a great many powders which are made for immediate use in blasting, especially when such powders are to be used in hot climates. The number of such blasting agents is almost infinite, and only a few need be mentioned in order to indicate their general character.

*Triumph Safety Powder (Courteille's).*—The composition of this powder is as follows:

Sodium nitrate .....	67.41	parts
Sulphur .....	11.23	"
Charcoal .....	7.75	"
Peat and coal .....	10.11	"
Metallic sulphates (combined).....	2.24	"
Oleaginous matter (animal or vegetable)	1.26	"

The several ingredients are pulverized and thoroughly incorporated in a dry state. The mixture is next saturated with steam, and finally subjected to the action of superheated steam until nearly dry, the temperature being gradually reduced from 250° F. to 150° F. The remaining traces of moisture are expelled by drying the powder on hot plates. The advantages claimed for this powder are freedom from explosion by friction or percussion, slow combustion due to the use of peat, charcoal, and hard coal, and finally it is claimed that the relatively great volume of gas evolved by the



gunpowder elements combines with the correspondingly small volume of the other ingredients, and under certain conditions, when the explosion occurs in a closed chamber or under pressure, tends to form *nitroglycerine* or other equivalent high explosives!

The absurdity of such a claim is manifest, and this mixture is mentioned merely as an example of many thousands of such explosives whose wonderful effects are developed only in the imagination of their inventors.

*Carbo-azotine, or Safety Blasting-powder.*—Several grades of this powder have been patented according to the nature of the work to be accomplished.

	Hard Rock.	Soft Rock and Hard Coal.	Soft Coal and Gypsum.
Potassium nitrate . . . . .	70.00	64.00	56.00 parts
Sulphur . . . . .	12.00	13.00	14.00 “
Lampblack . . . . .	5.00	4.00	3.00 “
Sawdust . . . . .	13.00	19.00	27.00 “
Ferrous sulphate . . . . .	2.00	2.00	5.00 “

The ingredients are ground or pulverized and boiled together in a weak solution of ferrous sulphate, the result being a liquid which gradually solidifies.

When nearly solid, the mass is thoroughly dried and granulated. The powder may be used in bulk, but is generally issued in the form of compressed cartridges, and requires strong confinement in order to develop its full force.

*Pyrolithe.*—The object of this mixture was to produce an explosive that would develop no carbonic oxide during combustion. Two grades have been patented, as follows:

Potassium nitrate . . . . .	51.50 . . . . .	18.00 parts
Sodium nitrate . . . . .	16.00 . . . . .	47.00 “
Sulphur . . . . .	20.00 . . . . .	17.00 “
Sawdust . . . . .	11.00 . . . . .	12.00 “
Charcoal . . . . .	1.50 . . . . .	“
Sodium carbonate or sulphate . . . . .	. . . . .	6.00 “

## LECTURE VI.

### GUNPOWDER—*Continued.*

**Properties of Gunpowder.**—Good gunpowder should be composed of hard angular grains which do not soil the fingers, and should have a perfectly uniform dark gray color. If the color is bluish or jet-black, the powder contains an excess either of charcoal or water.

The appearance of whitish or bluish-white specks or spots indicates that the nitre has effloresced during drying, or that the powder has absorbed sufficient water to partially dissolve the nitre which has accumulated on the surface, and in either case the incorporation is no longer uniform.

When new it should be free from dust, and a gramme of it flashed on a copper or porcelain plate should leave no residue or foulness. It should give the required initial velocity to the projectile, and produce not more than the maximum strain upon the gun. When exposed to air of average dryness it should not absorb more than from 0.5 to 1.5 per cent of water. In damp air gunpowder absorbs a much larger proportion of water, and deteriorates in consequence of the saltpetre being dissolved and crystallizing on the surface of the grains, while actual contact with water dissolves the saltpetre entirely and disintegrates the grains.

Prismatic powder should present a smooth surface, sharp, well-defined angles, and the prisms should not crumble along the edges when moderately rubbed. The size of the prisms and the diameter of the perforations may be measured by standard gauges for that purpose.

The property which exercises the greatest influence upon the general character of gunpowder, and the phenomena which attend its application as a propelling agent, is its *density*—*absolute density* or *specific gravity*. By density is meant the ratio which the weight of a given volume of the powder bears to the weight of an equal volume of water at 15°.5 C. It varies from about 1.50 to 1.85. On account of its importance, it would be well to consider this quality of gunpowder more closely. Density must not be confounded with hardness. A substance may be very hard and yet be of a low density. A powder with a very hard surface may be in reality less dense than another the surface of which is softer. Of course a very high density cannot be communicated without producing a considerable degree of hardness; but a powder may be made hard without rendering it very dense. Hardness seems to bear a direct relation to the power exerted in compressing, while density does not. Powder-dust containing about six per cent of moisture can be made very dense by the application of moderate pressure, while that containing one per cent can be brought to the same degree of density only by the exertion of enormous force; of these powders, the latter will be the harder.

Assuming the usual values assigned to the elements of gunpowder in the scale of specific gravities, the absolute density of a homogeneous mass of the mixture is 1.985. It is needless to say that this point is never reached in practical manufacture.

By subjecting powder-meal to powerful pressure its density is greatly increased, and consequently a given bulk of the pressed powder will yield on combustion a much greater volume of gas than an equal bulk of mill-cake. It becomes obvious, then, that the density of the powder which can be varied at will becomes its *most important* physical quality, on account of the great influence which it exerts on its action when ignited. It is evident that, if different amounts of material be compressed into equal bulks, the effect of equal amounts of the resulting powder, whether by weight or



volume, will not be equal. No experimental proof is necessary to show that if two grammes of powder of equal size, one of which is twice as dense as the other, be ignited in the open air, the denser will take a longer time to burn; for the former not only has a closer and less porous texture of grain, but contains a larger quantity of matter, bulk for bulk, to be burned from nearly the same surface, for in this case combustion occurs under the normal atmospheric pressure.

Under similar circumstances and conditions, differences in density may be assumed to effect the following changes in the manner in which a gramme of powder of average mammoth size is consumed in a gun:

*First.* On ignition it takes fire all over the surface, when, if sufficiently dense, it continues burning toward the centre in concentric layers until it is entirely consumed.

*Second.* If of too low density to resist the pressure to which it is exposed in the gun, the heated gases at once penetrate the pores, lighting their walls as they advance, thus causing a development of gas from a surface many times greater than that which may be called the original external surface.

It is therefore evident that uniformity of results and effect cannot be obtained in fired gunpowder, unless the density be uniform and constant from one discharge to another.

One of the most serious difficulties encountered in the use of gunpowder arises from the property of erosion. Although the erosive action of gunpowder occurs in the bore of small-arms, it is comparatively limited in extent and, with the older forms of powder, becomes perceptible only after continuous firing. With the more recent powders, however, and especially in guns of heavy calibre, this action of the powder-gases upon the bore often results from the firing of a single service round. For some years it was believed that the cause of trouble was to be found in the sulphur contained in the powder, and this belief was supported by the fact that among the products of combustion of gunpowder are to be found free sulphur and a mixture of potassium polysulphides

and potassium carbonate, which, at a bright red or white heat, exercise a powerful corroding action upon steel or iron. This action would naturally vary with the condition of the surface of the bore, temperature, pressure, and time of cooling.

Although sulphur may and probably does contribute to the erosive action of the powder-gases, the investigations of Nobel and Abel indicate that this is not the sole cause of trouble, but that an important factor is to be found in the passage along the surface of the bore of the highly heated and rapidly moving gases developed by explosion of the charge. Therefore, in order to eliminate this cause of trouble as far as possible, the nature and proportion of the ingredients of the powder should be such as to produce the greatest volume of gas with the least amount of heat, and the lowest pressure for the same temperature.

**Tests for Gunpowder.**—From what has been said, it is evident that certain defined physical and mechanical properties are essential in order that a uniform standard of results may be maintained, and that it is necessary that these points be determined with extreme accuracy and precision in the case of all military powders. The most important determinations to be made are:

1. The purity and proportions of the ingredients.
2. The hygroscopic quality of the mixture.
3. The thoroughness of incorporation.
4. The granulation and hardness.
5. The absolute density or specific gravity.

**Analysis of Gunpowder.**—A complete analysis of gunpowder includes the estimation of the ingredients, the determination of the nature of the characoal, and the degree of purity of the ingredients. When powder has been damaged by moisture or otherwise, or when a powder of new or unknown manufacture is to be examined, it should be tested qualitatively for various impurities suggested by the particular

cases under consideration, and the method of qualitative analysis to be adopted is determined by the results. A powder of known manufacture is examined qualitatively to determine the essential constituents and the chlorides and moisture. The following is the most reliable process. The determination of the nitre depends upon its solubility in water, while charcoal and sulphur are insoluble. That of sulphur depends upon its easy oxidation by means of fuming nitric acid and potassium chlorate, forming sulphates, which are estimated by precipitation as barium sulphate.

Three samples of gunpowder are weighed in rapid succession (in order that the percentage of moisture determined for one shall be true for all) in the following manner:

Two watch-glasses of equal size, with a clamp to fasten them together, are dried and weighed. A sample of powder (5 grammes) is then introduced and the whole reweighed: the difference is the weight of powder used. This sample (N) is placed in a beaker, of about 150 c.c. capacity, for the determination of the nitre. Another sample of powder of the same weight is introduced into the watch-glasses and weighed as before. This sample (S) is placed in a tall narrow beaker, of about 300 c.c. capacity, for the determination of the sulphur. A third sample of the same weight is introduced into the watch-glasses and weighed as before.

This sample (M) is placed, together with the watch-glasses and clamp, in a drying-oven, and dried, at not exceeding 60° C., for about 24 hours. It is then removed from the oven, the glasses are clamped, and the whole placed in the scale-case to cool. It is then reweighed. The loss of weight determines the *moisture*.

Sample N is covered with water (about 50 c.c.) heated to 100° C., and allowed to settle. Meanwhile two filters of the same size are prepared, and their difference in weight is determined. These are to form a double filter, the lighter being always placed underneath for convenience. A wide beaker, of about 300 c.c. capacity, is also weighed. The



clear portion of the solution is decanted on the double filter, and the filtrate received in the weighed beaker. The residue is again treated with boiling water and the operation repeated. The residue is then washed from the beaker upon the filter by means of boiling water, being careful that every particle of residue is rinsed out of the beaker. The filtrate is evaporated to dryness in a water-bath, heated to  $148^{\circ}$  C. in an air-bath, and weighed. The increase of weight determines the *nitre directly*.

The residue is dried on the filter at  $60^{\circ}$  C. and weighed on the upper filter, balancing this filter by means of the lower. The loss of weight, minus the difference in weight of the two filters, and corrected for moisture, determines the *nitre by difference*.

Sample S is covered with about 50 c.c. of fuming nitric acid, chemically pure, and brought to and maintained at a gentle ebullition. Small quantities of very finely pulverized potassium chlorate are added with caution, so that the liquid will not foam over, until a clear solution is obtained, being careful to add no more chlorate than is necessary for this purpose. If at any time there is a tendency to foam over, the beaker should be at once removed from the heat, and allowed to cool. The solution is allowed to cool and hydrochloric acid is added in small quantities at first from a pipette, then as the action decreases it is poured in, until the amount of liquid in the beaker is about doubled. The whole is evaporated to dryness, redissolved in about 50 c.c. of water, made up to exactly 100 c.c., which is usually a sufficient and convenient quantity, filtered, and the amount of sulphur ascertained by means of a decinormal solution of barium chloride. A normal solution is prepared by dissolving 244 grammes of the crystallized salt,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , in one litre of water; the decinormal solution is prepared by diluting a portion of this to ten times its volume.

To determine the sulphur, 5 c.c. of the solution containing the sulphates is put into a test-tube, and a portion of the

decinormal solution of barium chloride is added from a burette and the tube well shaken; when the precipitate has settled a drop or two more is added, and if cloudiness is produced more is added until the addition of a drop of barium chloride no longer produces cloudiness. Having thus approximately determined the amount of barium chloride required to precipitate the sulphates, a series of solutions of 5 c.c. of the solution of sulphates containing greater and less amounts of barium chloride is prepared. Thus if 7.2 c.c. was found to be the approximate amount required, the series would contain 6.8, 7.0, 7.2, 7.4, 7.6, 7.8 c.c. The precipitates are allowed to settle, and the tubes are tapped with the finger until the bubbles at the top disappear. A few drops of the solution of barium chloride are then poured in separate drops on a clean violet- or ruby-colored glass plate, and a few drops of the solution of sulphates on another portion of the plate. A drop of one of the clear solutions in the test-tubes, beginning usually with the lowest, is then put on the plate near one of each of the two solutions on the plate. One of the two drops thus placed is let into the drop of the solution of sulphates, the other into the drop of the solution of barium chloride, by means of a clean glass rod. If cloudiness appears in the sulphate solution, take the next higher (to which more barium chloride has been added), and so on; if cloudiness appears in the solution of sulphates, take the next lower (to which less barium chloride has been added), and so on, until a point is reached where no cloudiness is produced in either solution.

In making an analysis of U. S. regulation powders, the percentage of sulphur in the mixture being fixed as far as possible, the following method may be substituted for that just described, which, in practice, will be found to require very delicate manipulation. The amount of sulphur in these powders may be assumed to be 10 per cent, which for the amount under analysis (5 grammes) will be 0.5 gramme or 500 milligrammes.

From the reaction  $M_2SO_4 + BaCl_2 = BaSO_4 + 2MCl$  it is evident that every molecule of barium chloride detects one atom of sulphur; hence every cubic centimetre of normal solution of barium chloride (since it contains a number of milligrammes of barium chloride equal to its molecular weight) is equivalent to a number of milligrammes of sulphur equal to its atomic weight, or 32. Every c.c. of a decinormal solution will then be equivalent to  $\frac{32}{10}$  mg. sulphur. There were 100 c.c. of the solution of sulphates, 5 of which were used in the determination; hence  $\frac{32}{10} \times 20 \times$  the number of c.c. of barium chloride solution used determines the weight of the *sulphur* in milligrammes.

To determine, then, the several amounts of  $BaCl_2$  to be added to each test-tube in order to form the first approximate series, we may substitute in the last expression

$$\frac{32}{10} \times 20 \times x = 500, \quad \text{or} \quad x = 7.8.$$

Hence we may now make our first approximation by adding to the six tubes in succession 7.4, 7.6, 7.8, 8.0, 8.2, and 8.4 c.c. respectively. They are then placed in a test-tube holder and the precipitates allowed to settle. A few drops of the  $BaCl_2$  solution are then introduced into each tube by means of a pipette until two consecutive tubes are found, in one of which an additional precipitate of  $BaSO_4$  is formed, while the other remains perfectly clear.

The result of this operation, which consumes but a few minutes, enables us to form a second series of solutions of 5 c.c. each, in which the approximation is so close that the result may be accepted as practically exact. Suppose that, as a result of the first approximation, the two consecutive tubes were those in which 7.8 and 8.0 c.c. of the  $BaCl_2$  solution had been added. We then proceed to form a second series of solutions by adding 7.7, 7.8, 7.9, 8.0, 8.1, and 8.2 c.c. of the  $BaCl_2$  solution to the several tubes in succession. Allow the precipitates to settle, and proceed as before. In this way the degree of approximation is very close, while in



practice it has been found much easier to detect the exact point at which all of the  $\text{BaSO}_4$  has been precipitated than in the manner previously described.

The charcoal may be determined (*a*) as follows: The filter containing the sulphur and charcoal after the nitre has been extracted is thoroughly moistened with warm water, and the neck of the funnel containing the filter closed temporarily with a cork.

The residue on the filter is moistened with alcohol, and then covered with carbon bisulphide and allowed to digest for two hours, covering the funnel with a ground-glass plate. At the end of two hours the liquid is drawn off, and the process of digestion repeated until a drop of the liquid evaporated upon a piece of clean platinum-foil leaves no residue. The filter is dried and weighed, and the difference in weight between the filter alone and the filter with residue will be the weight of charcoal. By collecting the bisulphide solution in a weighed flask, evaporating upon a water-bath at between  $70^\circ$  and  $80^\circ$  C., further heating the contents of the flask up to the point of fusion, and driving off the carbon bisulphide vapors by a current of dry air, the weight of sulphur may be very closely determined, the slight error being due to a small percentage of allotropic sulphur present in the powder which is insoluble in carbon bisulphide.

The charcoal may also be determined (*b*) by extracting the nitre from one sample and subtracting from the weight of the residue that of the sulphur found in an equal weight of another sample.

The chlorides are determined by redissolving the nitre obtained in the estimation of nitre by the direct method in the smallest quantity of water, and proceeding as in the estimation of chlorides explained under Nitre.

The following example will illustrate the method of analysis just described and the form of record:

## DEPARTMENT OF CHEMISTRY AND EXPLOSIVES.

## ANALYSIS OF GUNPOWDER.

FORT MONROE, VA, April 22, 1889.

*Kind of Powder:* Hexagonal, E. V. D. (Du Pont).

Milligrammes.

Weight of watch-crystals + clamp.....	19804	
Weight of watch crystals, clamp + powder.....	24804	
Weight of watch-crystals, clamp + powder dry.....	24745	
Moisture.....	59	
Percentage of <i>moisture</i> , 5000 : 59 :: 100 : $x$ =		1.18 per cent.
Weight of powder corrected for moisture.....	4941	
Weight of beaker + nitre.....	86961	
Weight of beaker.....	83300	
Weight of nitre— <i>direct</i> .....	3661	
Percentage of <i>nitre (direct)</i> , 4941 : 3661 :: 100 : $x$ =		74.094 per cent.
Difference in weight of filters + residue.....	1334	
Difference in weight of filters.....	50	
Weight of residue.....	1284	
Weight of <i>nitre—by difference</i> (4941 - 1284).....	3657	
Percentage of <i>nitre (by difference)</i> , 4941 : 3657 :: 100 : $x$ =		74.013 per cent.
Weight of powder corrected for moisture.....	4941	
Sulphate solution measures 110 c.c.		

Amount tested, 5 c.c., required 7 7 cc.  $\frac{A}{10}$  BaCl<sub>2</sub>.

Weight of sulphur, $7.7 \times 0.0032 \times 22 =$	542	
Percentage of <i>sulphur</i> , 4941 : 542 :: 100 : $x$ =		10.971 per cent.
Weight of residue.....	1284	
Weight of sulphur.....	542	
Weight of charcoal.....	742	
Percentage of <i>charcoal</i> , 4941 : 742 :: 100 : $x$ =		15.015 per cent.
Percentage of nitre (direct).....	74.094	(by diff.) 74.013
Percentage of sulphur.....	10.971	10.971
Percentage of charcoal (a).....	14.945	(b) 15.015
	100 000	99.999

**Determination of the Hygroscopic Quality of the Powder.**—The amount and percentage of moisture in the powder is determined as has just been described in the analysis of gunpowder. The ability to resist moisture is determined by subjecting samples of the powder, which have been dried, to exposure, first, in the open air; second, in the hygroscope containing a solution of saltpetre made at 100° and cooled down to 80° F.

The hygroscope is an air-tight box arranged to contain specimens of powder, while subjecting them to a damp atmosphere at nearly uniform temperatures for 24 hours. It consists of two parts, an inner compartment of copper (about 12"  $\times$  12") and the outer case of wood, the two being separated by a space of two inches which is solidly packed with hair. The top or lid is also double and made non-conducting by hair packing, the lower face being of copper and fitting closely to the sides of the inner compartment. As an additional precaution, an india-rubber gasket extends around the top of the outer case, and the top is drawn into very close contact with this by means of thumbscrews. A movable tray of copper, the bottom of which is perforated, rests upon projections from the walls of the inner compartment.

The powder to be tested is placed in circular cups, one inch in depth and three inches in diameter, which are fitted with wire-gauze bottoms of sufficiently small mesh to contain the finest-grained powder. The percentage of gain is determined by weighing in carefully prepared bottles, into which the powder is introduced as soon as the hygroscope is opened.

The influence of atmospheric conditions on the quantity of moisture absorbed by the powder is so great that accuracy requires that a careful record be kept of the barometer, hygrometer, external thermometer, and of a maximum and minimum thermometer, fitted inside of the hygroscope whenever samples are being tested, and in each case reference should be made to tables previously worked out in the case of a standard powder of like specific gravity, and granulation under like conditions.

**Test for Proper Incorporation.**—Thoroughly incorporated powder presents a perfectly homogeneous appearance, and upon breaking up a granule it should show an ashen-gray color, and the texture should be very close; a granular appearance, and especially the presence of any white specks, is inadmissible. This examination should be made with the assistance of a magnifying glass.

The flashing of a gramme or so of the powder on a copper



or porcelain plate has been alluded to; but to form an accurate judgment, and especially to compare the degrees of incorporation of different powders, by this test, requires great care and experience. As an improvement upon this rather crude test, Colonel Chabrier proposed what he termed a "Pyrographic Method for the Examination of Gunpowder." This method consists in flashing the powder on sheets of paper colored blue with iodide of starch, the result being a bleaching of the paper in spots and streaks. From the size, shape, and general appearance and arrangement of the spots and streaks, the character of the powder is determined.

This process is an advance upon the original one, but practically considerable difficulty was encountered in the preparation of the paper before use, and the preservation of the record thereon after the test had been applied.

The following method of applying the "Flashing Test" has been proposed by Professor Munroe of the U. S. Naval Torpedo Station, and has given excellent results.

Instead of the iodide-of-starch paper, he employs a paper colored with Turnbull's blue, which is decomposed (and its color thereby destroyed) by solutions of the alkalies and the alkaline carbonates. The alkaline sulphides and thiosulphates also act upon this paper with the partial production of a yellow color; therefore by flashing gunpowder upon such paper yellow and white spots will be formed. The test is made as follows:

Pieces of the paper, 6 or 8 inches square, are dampened and placed on a glass or porcelain plate. A small truncated leaden cone (3 grammes in capacity) is closed at the smaller end with the finger and filled evenly with the powder to be tested. The powder is placed upon the paper by inverting the cone carefully so as to produce a conical heap, which is immediately fired either by a heated iron or copper wire, or, better still, by a fine platinum wire heated to incandescence by an electric current. The paper is exposed to the action of the residue for 30 seconds, and then washed in running water.

When pulverized mill-cake is flashed in this way, the

space described by the base of the cone will be blackened and partially bleached by the dampened layers of powder in contact with it; next above this space will be black smutches and streaks, while the whole surface of the paper will be covered with white and yellow spots. With badly incorporated powders these spots are coarse and irregular in shape and distribution, while in the case of thoroughly incorporated powders the spots are fine and so evenly distributed over the surface of the paper that it appears merely of a paler color with occasional spots and streaks.

**Granulation and Hardness.**—The size of the grain is determined by standard sieves made of sheet brass. Two sieves are used for each kind of powder, and the diameters of the holes are as follows:

Kind of Powder.	No.	Diameter.	No.	Diameter.
Musket.....	1	0".03	2	0".06
Mortar.....	3	0".10	4	0".25
Cannon.....	5	0".25	6	0".50
Mammoth.....	7	0".75	8	0".90

The dimensions of the special powders have been given elsewhere. The shape of the grains can be judged only by the eye, but the more recent powders belong to the class known as Powders of Regular Granulation and are very uniform in shape; however, a compact shape approaching a cube or sphere is preferable, and elongated flat scales are very undesirable. The hardness can be determined only approximately, since the hardest-grained powder is considerably below any scale used for determining this quality. Experience in this matter is the only guide, and it is a very difficult thing to determine the relative hardness of the various powders.

On account of the importance of the exact determination of the density of powder, I have decided to devote an entire lecture to that subject, and will merely add a few words of precaution as to the care of gunpowder.

**Preservation, Storage, and Transportation of Gunpowder.**—Before leaving the subject of gunpowder, it remains to add a few precautions as to its preservation, storage, and transportation. Government powder is packed in barrels of 100 pounds each. Powder-barrels are made of well-seasoned white oak and hooped with hickory or cedar hoops, which should be deprived of their bark. The hoops should cover two thirds of the barrel. Instead of a bung on one side, a screw-hole  $1\frac{1}{2}$  inches in diameter is made in the head of the barrel for mortar- and musket-powder; it is closed by a wood-screw with an octagonal head which must not project beyond the ends of the staves; under the head of the screw is a leather washer steeped in a solution of beeswax in turpentine. The interior of the barrels may be lined with paper, painted or shellacked to render them more impervious to moisture.\*

For transportation, a piece of cloth should be glued over the head of the screw. Powder-barrels may be hooped with copper; and boxes lined with galvanized iron and copper with large screw-lids have also been tried as substitutes for the ordinary barrel. The heads of each barrel are painted black, and on them are marked (in white oil-paint) the number of the barrel, the name of the manufacturer, the year of fabrication, the kind of powder, the mean initial velocity, the pressure per square inch, and the density. The barrels should be placed so that marks on each can be easily seen.

In Germany the kind of powder contained in a barrel is plainly shown by means of different-colored labels; those containing rifle-powder have yellow, cannon-powder red, and meal-powder white labels.

In powder-magazines the barrels are generally placed on their sides, three tiers high, or even four tiers if necessary. Small skids should be placed on the floor and between the

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\* In 1780 a curious and interesting experiment was tried in Hanover with the view of protecting the contents of powder-barrels from moisture. Barrels containing powder were covered by pasting on the outside well-glued paper that had been soaked in alum and then dipped into pitch. The barrels were then immersed in water for a month, and upon examination the powder was found to be unimpaired.



several tiers of barrels in order to steady them, and chocks should be placed at intervals on the skids to prevent the rolling of the barrels. The barrels should be turned at least once in three months to prevent the powder from caking. This is done by taking down one or two barrels from each row, and rolling the rest back and forth, and then replacing the barrels which had been removed.

The powder should be separated according to its kind, the place and date of fabrication, and the proof range. Fixed ammunition, especially for cannon, should not be put in the same magazine with powder in barrels, if it can be avoided.

Igniters, fuzes, detonators, primers, percussion-caps, fireworks, etc., should never be stored in powder-magazines.

In a room 13 or 14 feet wide the barrels may be arranged in a double row in the centre, two alleys  $2\frac{1}{2}$  feet wide, and two single rows 6 to 12 inches from the walls; in this way the marks of each barrel may be seen, and any barrel can be easily reached. In a room 12 feet wide an equal number of barrels may be placed in two double rows, with a central alley of 3 feet, and two side alleys, next the walls, of about 10 inches each. There should be an unencumbered space of 6 or 8 feet at the door or doors of the magazine.

Should it be necessary to pile the barrels more than four tiers high, the upper tiers should be supported by a frame resting on the floor; or the barrels may be placed on their heads, with boards between the tiers.

Besides being recorded in the magazine book, each parcel of powder should be inscribed on a ticket attached to the pile, showing the entries and the issues.

For the preservation of the powder and of the floors and lining of the magazine, it is of the greatest importance to preserve unobstructed the circulation of air under the flooring as well as above. The magazine should be opened and aired in clear dry weather, *when the temperature of the air outside is lower than that inside the magazine*. It should not be opened in damp weather if it can be avoided. The ventilators must be kept free; no shrubbery or trees should be allowed

to grow so near as to protect the building from the sun. The magazine yard should be paved and well drained. The moisture of a magazine may be absorbed by chloride of calcium suspended in an open box under the arch, and renewed from time to time; quicklime is dangerous and should not be used.

The sentinel or guard at a magazine, when it is open, should have no fire-arms, and every one who enters the magazine should take off his shoes, enter barefooted, or wear slippers made of buckskin; no sword or cane or anything which might occasion sparks should be carried in.

The windows should have inside shutters of copper wire-cloth. Fire should never be kindled near the magazine for the repair of the roof or lightning-rods.

Barrels of powder should not be rolled for transportation; they should be carried in hand-barrows, or slings made of rope or leather. In moving powder in the magazine a cloth or carpet should be spread; all instruments used there should be of wood or copper, and the barrels should never be repaired in the magazine.

In the spring an inspection of the barrels should be made, and the hoops swept with a brush wherever they can be got at, to remove the insects which deposit their eggs at this season.

In wagons, barrels of powder must be packed in straw, secured in such a manner as not to rub against each other, and the load covered with thick canvas.

In transportation by railroad, each barrel should be carefully boxed and packed, so as to avoid all friction. The barrels should have a thick paulin under them. The cars should have springs similar to those of passenger-cars.

## LECTURE VII.

### DENSIMETRY.

DENSIMETRY is the term applied to the operation of determining the density of gunpowder, the apparatus used being known as densimeters. In this connection the term *density* has itself been loosely applied, and has been variously understood to refer to the relative, absolute, or gravimetric density of gunpowder. In the earlier attempts to determine the relative density of powders, liquids exercising the minimum solvent effect upon the powders were tried, but only approximate results were obtained.

One of the first efforts consisted in filling a carefully calibrated and graduated glass jar with absolute alcohol until the liquid occupied a certain volume, and after allowing sufficient time for any drops adhering to the sides of the jar to run down, and carefully noting the volume occupied, a weighed quantity of powder was introduced into the jar by means of a wide-stemmed glass funnel, and the new volume occupied by the alcohol and powder was noted. From the data thus obtained it was assumed that the relative density or specific gravity could be easily calculated.

With all possible care, however, this method was but a crude approximation on account of the absorption of the alcohol by the grains of powder with the consequent expulsion of air from the pores of the grains caused by this absorption. According to the character of the powder, whether glazed or unglazed, tough or porous, the action of the alcohol was more or less rapid, and therefore, according to the operator and the time consumed in the operation, the relative



density varied so that a powder of very low density was made to appear to have an extremely high one, or the reverse.

Various other methods were proposed and tried, and numerous densimeters were invented, notably Marchand's, Hoffmann's, Bode's, Ricq's, and others, all of which possessed merits, but generally counterbalancing defects. The first practical densimeter by means of which reliable and uniform results were obtained was invented by Bianchi, and in a modified form is still used under the name of Mallet's Mercurial Densimeter.

**The Mallet Densimeter.**—This apparatus is used at the Artillery School for the determination of the density of rifle-, mortar-, and cannon-powders used in field-guns. It consists of a small table to one end of which is firmly secured an iron standard, to which is attached a barometer-tube of peculiar make; instead of being of a single piece and closed at the upper end, it is made of two separate pieces and open at the top. The upper part is about 24 inches in length and is connected to the lower, which is 10 inches in length, by means of a closely fitting and perfectly air-tight screwed metal joint; the lower part, instead of being a plain parallel tube of the same diameter throughout as the upper, is made in the form of a globe or bulb (*vase*). To each end of this globe is attached a metal collar fitted with female screw-threads, and the connections between the barometer-tube above and the nozzle below are by metal plugs accurately fitted to these threads. The upper plug is fitted with a fine gauze diaphragm, which prevents grains or particles of powder from entering the upper part of the tube, while the lower plug is similarly fitted with a diaphragm of chamois-skin, which strains and cleans the mercury before it enters the globe. The nozzle mentioned above screws into the lower plug and dips into the mercury. The lower extremity of the upper part of the tube and both plugs are fitted with air-tight stop-cocks.

The mercury is contained in a heavy porcelain dish which can be raised or lowered by means of a hand-screw, so as to

keep the tip of the nozzle immersed to the proper depth. The upper part of the tube is attached to a scale, which in turn is attached to the standard. To the opposite end of the table is attached an air-pump of ordinary construction. The vacuum-gauge is in an air-tight glass case, which is placed between the standards on which the brake works; it can be shut off from connection with the cylinder by a stop-cock, and air is admitted to it and thence to the cylinder, etc., by unscrewing the glass cover, which can be turned by means of a chamfered ring on the brass collar into which it fits.

Connection with the *densimeter* is controlled by a stop-cock under the bell-glass table. The cylinder (of brass) oscillates on trunnions at its base; its connections with the vacuum-gauge and the *densimeter* are by means of rubber hose. The cylinder-head is fitted with an oil-hole closed by a screw-plug, and has an overflow-can to catch the oil forced out in exhausting. To prevent any mercury which might find its way from the top of the barometer-tube from flowing into the air-pump, the densimeter and air-pump are connected by hose through the medium of a "catch-bottle," into which the escaping mercury may overflow without damage.

The *balance* employed in connection with the densimeter is a beam-scale constructed with great accuracy. It consists of a beam of brass mounted on a hollow standard with ordinary scale-pans. The beam and scale-pans are supported on steel knife-edges. The beam, when not in use, rests upon the top of the standard, the weight of the scale-pans being taken from their knife-edges by the base of support of the standard. The central knife-edge, when the beam is not in action, rests in V's in the head of the standard, but bears no weight. The beam is thrown in and out of action by means of a lever at the foot of the standard, which acts on a stout rod running up through the standard. To the upper extremity of this rod is attached a double cross-head, the upper surfaces of which are faced with polished hardened steel, and on these surfaces the pivoting or central knife-edge rests in weighing. A pointer extends from the beam downwards,

and the oscillations are marked by a scale attached to the foot of the standard. To the base of support is attached a German level, and the base itself is furnished with levelling-screws, by means of which the apparatus may be levelled.

**Precautions to be Observed in Using the Densimeter.—**

1. As all of the different connections of the globe, where air-tight joints are made, are fitted with leather washers of constantly changing thickness, it follows that a variable degree of screwing up is required in order to make the junctions absolutely perfect. With the plugs which screw into the ends of the globe, it is of great importance that the extent to which they enter should be uniform for any given number of trials with the same powder; that is, they should be run in to the same distance when each sample of powder is tried that they were when the globe was filled with mercury alone, for if not in far enough the capacity of the globe is increased, and if in too far it is reduced.

In order to eliminate this source of error as far as possible, set-marks are put on the collars and plugs. So long as these are either brought together or kept separated by a fixed and constant amount during the different trials, the experiment will be accurate. As coincidence will probably only occur when the washers are new, the separation as they wear away or become compressed must be determined for the several trials from which the determination of the density of any given sample of powder is to be calculated, and retained throughout those trials.

2. In screwing on the nozzle and in screwing in the plugs, both wrenches should be used—one as a spanner, to hold against the other used as a wrench, otherwise the cementing of the collars may be started and leaks produced. Attached to the table of the densimeter used at the Artillery School is a seat so arranged with projecting studs that the globe may be placed therein and firmly held by the collars while the plugs and nozzle are being attached to or detached from the globe, so that all wrenching or twisting is removed from the cemented joints between the globe and collars.



3. The zero of the scale attached to the upper part of the barometer-tube is *the lower end of the nozzle*. The quantity of mercury in the dish and the level on which the dish rests should be so regulated that the immersion of the nozzle will not be greater when the globe is full than is necessary to prevent the admission of air. This is necessary in order to avoid fluctuations in the height of the barometric column, which are misleading as to the condition of the instrument.

4. When leaks in the connections of the globe occur they are indicated by air-bubbles, which can be distinctly seen passing up through the enclosed mercury. They can generally be located, if about the junctions, by closing the cocks in succession, beginning at the lowest and exhausting at the same time by means of the air-pump. If the leak be about the tube-connections, the air will continue to flow with all the cocks closed; if it be below this point, it can be located between the cocks. By tightening the junctions with the wrenches, or, if in the cocks, by screwing them up with a screw-driver, the difficulty is remedied.

It sometimes happens that the cement which holds the collar to the neck of the globe becomes cracked and produces a leak; this can be located by filling the globe, closing both cocks, and expanding the mercury by wrapping a warm cloth around the globe; globules of mercury will be forced out at the point where the leak exists. By exhausting the globe and at the same time applying to the leak semi-melted beeswax, or a mixture of beeswax and tallow, the leak can be stopped.

5. When the globe is detached after it has been filled, every particle of mercury adhering to the plugs must be carefully removed by jarring or brushing. This precaution is very important. The mercury that thus adheres at different trials varies; therefore the accuracy of the weight taken is sensibly affected if care is not taken to remove all traces of mercury outside of the cocks. For the same reason any globules of mercury adhering to the globe and its connections should be removed by brushing before weighing. In testing fine-grained powder both plugs should be unscrewed and,

with the globe, carefully wiped out after each trial; with ordinary cannon-powder this need be done only occasionally.

6. Whenever the upper part of the barometer-tube or globe becomes coated with sulphuret of mercury it should be dismounted and washed with *aqua regia*. Should the upper part of the barometer-tube be broken, expose the metallic socket which holds the lower end to the flame of a lamp until the cement softens, remove the broken tube and replace the socket. Coat the end of the new tube with cement, and insert it in the socket before the mixture cools, being careful that the tube stands vertical, and attach it to the scale.

7. The following precautions are necessary in using the air-pump: Always keep the piston-rod and piston well oiled; keep the stop-cocks and connections air-tight; screw down the vacuum-gauge before beginning to exhaust; examine the hose connections from time to time. To determine whether the pump is tight and in working order, close the cock under the bell-glass table and exhaust. The vacuum-gauge will show whether air is admitted, and the leak may be located by the hissing sound made by the air rushing in.

8. The following precautions are to be observed in using the balance: Always lower the beam before putting the globe or the estimated counterbalancing weights on the pans, and also before removing either of them. The small weights may be added or changed with the beam in action. Always place the heavier weights in the centre of the pans so as to avoid any tendency to swing the beam laterally. In throwing the beam into action, use a gentle regular motion. The oscillations when the balance is nearly in equilibrium may be checked by gently lowering the beam and pans into their rests until the motion ceases. When again raised, the beam will be quite steady, and exact equilibrium will be easily established.

**The Process of Determining the Density of a Sample of Powder.**—The connections of the instrument having been previously tested and everything found in working order, the globe, with the nozzle attached, is carefully brushed and

connected to the upper part of the barometer-tube. The bowl containing the mercury is raised by means of the elevating-screw, until the tip of the nozzle is immersed to a sufficient depth to prevent any air getting into the globe. The lower stop-cock is closed, all the others are opened, and the air is exhausted from the globe and tube by means of the air-pump. As soon as a perfect (or nearly perfect) vacuum is obtained, as shown by the vacuum-gauge, the lower stop-cock is opened.

The mercury immediately rises into the globe, and, as the level of the mercury in the bowl falls, great care must be taken to keep the tip of the nozzle constantly immersed to a uniform depth by means of the elevating-screw. As soon as the column of mercury becomes stationary (it should rise in an unbroken column to about the usual barometric height), the lower stop-cock is closed. Air is then admitted to the top of the tube by opening the stop-cock attached to the catch-bottle, which will cause a very slight fall in the mercury column. The other stop-cocks of the globe and tube are then closed, the globe carefully disconnected, placed in its seat on the table, the nozzle removed, and all traces of adhering mercury jarred and brushed off. The globe filled with mercury is then very carefully weighed and the weight noted (*W*). The globe is next emptied, the mercury being returned to the bowl, and the upper plug of the globe removed so that the sample of the powder can be introduced.

For many practical reasons it has been found convenient to use a constant, uniform weight of powder, the weight adopted at this school being 9 ounces, or 3937.5 grains. The sample, carefully weighed, is introduced into the globe, the nozzle attached, and the globe again connected with the rest of the instrument. The cock at the lower end of the upper part of the tube is opened to allow the mercury remaining in it to escape, the catch-bottle and nozzle stop-cocks closed, and the air is again exhausted.

The mercury is run into the globe and up to the same point in the tube as before, the cock closed, air admitted, and



the globe disconnected, cleaned and weighed as before. This weight ( $W'$ ) is also noted. As during the experiment the temperature of the mercury has varied (due to the rapid manipulation), its temperature should be determined at the beginning of the experiment and after each weighing, and the mean of the three thermometric readings taken as the true temperature, corresponding to which the specific gravity of the mercury is to be taken in the subsequent calculation. From the data thus obtained the density of the powder is readily obtained from the proportion

$$D : d :: W - (W' - w) : w,$$

or

$$d = \frac{D \times w}{W - (W' - w)},$$

in which  $D$  = the density of the mercury corresponding to the temperature noted;

$d$  = the density of the powder to be determined;

$W$  = the weight of the globe filled with mercury alone;

$W'$  = the weight of the globe filled with mercury and powder;

$w$  = the weight of the sample of powder taken.

Evidently  $W - w$  represents the weight of mercury, globe, and powder less the weight of powder taken, and  $W - (W' - w)$  the weight of mercury displaced by the powder.

It is very important in these experiments that the mercury should be of the proper quality, and in addition to straining it through chamois-skin from time to time, to remove any impurities, its specific gravity should be tested. At 66° F., or 18°.9 C., it should have a specific gravity of 13.55055.

**The Dupont Densimeter.**—For the determination of the density of large-grained powders, the instrument in use at the

Artillery School was constructed according to the plan of one designed by the Dupont Powder Company, and employed by them with very satisfactory results at their works near Wilmington, Del..

It is a mercury densimeter, adapted, by its construction, to the reception of large grains, and having capacity for five pounds of powder, which, for convenience, is the weight of sample always employed. It differs, however, from the small densimeter just described by a combination of the different parts such that the reservoir for holding the powder and mercury to be weighed, and the balance by means of which the weighings are made, are assembled together in one instrument. The balance also is so adapted to its special purpose as to simplify considerably the subsequent process of calculation.

A great saving of time and labor is gained by this form of instrument, and the occurrence of breaks and leaks, so frequent in the small apparatus, is in a great measure avoided.

The instrument is enclosed in a case about seven feet long by two feet wide and six feet high, built upon a solid brick support, access to the instrument being had through double doors which, when open, expose one entire side.

The instrument consists essentially of three parts, viz., a beam-scale, a reservoir to contain the powder and mercury to be weighed, and a bowl to contain the mercury when not required in the reservoir.

The *beam-scale* is suspended from a hook firmly secured to the top of the case, and its axis of suspension is a knife-edge lying in the same plane with the axis of suspension of the reservoir and of the rods to which are attached the platforms on which the weights are placed. The latter consists of pounds, tenths of a pound, and five-hundredths of a pound, *marked with reference to the weights they will balance in the reservoir*, and of a large unmarked weight, termed the *counterpoise*.

This counterpoise has a cavity bored in it lengthwise, the use of which will appear hereafter; its weight is about eight

pounds. The long arm of the beam is also graduated, and by means of a " rider " the weighings can be made to hundredths and thousandths of a pound; the graduated edge of the beam is in the same plane with the knife-edges. Attached to the upper edge of the beam are two small counterpoises which admit of movements parallel and perpendicular to the beam respectively, the movements being regulated by screw-spindles passing through the counterpoises. The one having the parallel or horizontal motion is just over the axis of suspension of the beam, and is used to adjust the arms to the same weight; the other, having the perpendicular or vertical motion, is attached to the shorter arm, and its function is to regulate the sensibility of the balance. The beam and its appurtenances are of brass.

The *reservoir* is of cast iron, and consists of two conical ends which screw into a cylindrical section. These joints are fitted most accurately, lest ledges should be formed within the reservoir which might serve to retain enough mercury to affect the weighings. Attached to the top of the reservoir is a small detachable glass vase into which the mercury rises when the reservoir is filled, and which enables the operator to mark the exact point to which it must be filled for any given experiment. A nozzle, fitted with an air-tight stop-cock, screws into the lower conical section.

The reservoir swings on trunnions, the beds for which are at the lower extremities of a yoke attached to the beam. The upper part of the yoke is fitted with a vertical pivot, by means of which, in addition to a vertical or up-and-down motion, the reservoir may be given a horizontal angular movement.

The powder is introduced into the reservoir through a circular mouth about  $2\frac{1}{2}$  inches in diameter in the upper conical section.

A screw-cap, fitted with a soft leather washer, covers the mouth, and when removed, for the purpose of introducing the powder, is hung on a hook attached to the right-hand side of the yoke, so as to be included in the weighing. The mer-



cury is admitted to the reservoir and withdrawn through the nozzle already mentioned.

The capacity of the reservoir is about 78 pounds of mercury alone, or 40 pounds of mercury and 5 pounds of powder. The reservoir itself weighs  $20\frac{1}{2}$  pounds.

The *bowl* is also of cast iron, and has a capacity for about 110 pounds of mercury. By means of an elevating-screw, worked by a wheel, it can be raised or lowered so as to keep the tip of the nozzle always immersed at a uniform depth. Near the bottom of the bowl, and to one side, is an outlet-pipe, by means of which the mercury can be withdrawn when the instrument is not in use.

In connection with this densimeter is used an ordinary Ritchie air-pump, in which, the cylinder remaining stationary, the oscillation takes place in the connecting-rod, which communicates the motion of the handle to the piston. The air-pump and densimeter are connected through a catch-bottle by means of rubber hose.

**Precautions to be Observed in Using the Dupont Densimeter.**—After the instrument has once been put in thoroughly good working order, serious injury to it can result only from very rough treatment. However it is well to observe the following precautions:

1. In removing the reservoir from the yoke, disconnect the rubber hose from the glass vase, revolve the reservoir on its trunnions until it is inclined about  $30^\circ$  from the vertical, and then raise it obliquely and *very gently*, so as to avoid any jar or shock upon the knife-edges of the beam. To replace it, be equally careful.

2. When removed in order to brush the globules of mercury, place the reservoir on a table so that it rests on its sides, and, having taken off the screw-cap, brush out the interior carefully, inverting the reservoir to allow the mercury to run out. A slight jar will free the nozzle from any particles of adhering mercury. Always examine the screw-threads on the cap, as a few globules of mercury always find their way into them.

3. The joint between the glass vase and the metal top of the reservoir is very delicate and difficult to keep perfectly air-tight. Therefore be particularly careful not to strike the vase, or jar it in any manner, especially in removing or replacing the rubber hose. The latter should always be brought from the catch-bottle over the hook to which the beam is attached.

4. It is not necessary to use force to make the screw-cap joint air-tight, provided the leather washer is not worn out. The exercise of a very gentle pressure on the wrench is sufficient.

5. When running the mercury into the reservoir, keep the nozzle immersed at such a constant uniform depth as to prevent any air from getting into the instrument. As it will be found necessary to continue to exhaust the air until the mercury has risen to the proper level, care should be taken to work the brake with uniform strokes so that the flow of mercury may be regular.

6. The process of weighing is often a very important operation on account of the extreme sensibility of the beam-scale. As there is no way of arresting the vibrations except by the hand, when equilibrium is nearly produced, it is convenient to arrest the vibrations by holding the thumb and forefinger of the right hand a little below and above the support for weights attached to the longer (right) arm of the beam, while with the left hand the "rider" is manipulated until equilibrium is produced.

7. The precautions necessary for the proper care of the air-pump have already been enumerated. To preserve the reservoir from rust while the instrument is not in use, it is covered with a light coat of paraffin, which can be readily removed by holding it over a flame.

**To Determine the Density of Powder with the Dupont Densimeter.**—The reservoir having been carefully cleaned and placed in the yoke, the beam is accurately balanced by means of the counterpoise used for that purpose, and the eight-pound counterpoise placed on the left-hand support.

The bowl is then filled with mercury and run up by means of the elevating-screw until the tip of the nozzle is immersed to the proper depth. The densimeter is then connected with the air-pump, the nozzle stop-cock closed, and the air exhausted by the air-pump.

As soon as the gauge indicates a vacuum, the stop-cock is opened and the mercury rises in the reservoir, the air-pump in the meantime being worked constantly and uniformly. When the mercury column reaches the proper height in the vase the stop-cock is closed, the hose disconnected, and the point at which the mercury stands marked by a wire used for the purpose. (When the hose is disconnected, it sometimes happens that the mercury column falls too low to be marked by the wire; in this case a little mercury is poured into the tube from the top, and the point marked as before. Occasionally a little mercury has to be run off, which can be done by carefully opening the stop-cock until the mark is reached.)

The balance of the beam is now restored by dropping small shot into the cavity of the counterpoise, the weight of the latter being slightly less than the reservoir when filled with mercury alone; this having been done, the stop-cock is opened and the reservoir emptied.

The reservoir is removed from the yoke, the screw-cap taken off, and all particles of mercury carefully brushed and *jarred* out; it is then replaced in the yoke, the cap hung on the hook, and, the large counterpoise having been removed, the equilibrium of the beam is verified.

The five-pound weight is now placed upon the left-hand support, and the sample of powder introduced into the reservoir until equilibrium is again restored.

The screw-cap is then replaced, the large counterpoise added to the five-pound weight already on the left-hand support, and the reservoir filled with mercury, by means of the air-pump, to the same height as before. The rubber hose is again disconnected from the vase, and equilibrium for the fourth time restored by placing weights on the right-hand platform (attached to the longer arm of the beam), and, in



addition, by manipulating the "rider" on the beam if necessary. The sum of these weights is the weight of the mercury displaced by the powder, or of a volume of mercury equal to the volume of the powder, and the specific gravity, or *density*, of the latter results from the well-established principle that "*the specific gravities of two substances are proportional to the weights of equal volumes of those substances.*"

As the density of mercury varies with its temperature, and this temperature varies during each experiment, it is necessary to determine the temperature of the mercury at the beginning of the experiment and each time that the reservoir is emptied, and the mean of the thermometric readings taken as the temperature corresponding to which the specific gravity, or density, of the mercury is to be taken in the subsequent calculations.

Thus if  $D$  = the density of the mercury corresponding to the observed temperature;

$d$  = the density of the powder to be determined;

$W$  = the sum of the weights on the longer arm;

$w$  = the weight of the powder,—

then, according to the principle enunciated,

$$D : d :: W : w,$$

or

$$d = D \frac{w}{W}.$$

In this densimeter not only are the weighings rapidly and accurately made, but the actual weights required for the computation are obtained directly by a process peculiar to the balance.

*The weights for the longer arm are marked double their actual value in reference to the reservoir, so that in computing the density of any sample of powder it is only necessary to place the decimal point in the value of  $D$  one place farther to the right, and divide by the value of  $W$ , as indicated on the*

*weights*, which is evidently the same thing as multiplying both terms of the fraction  $\frac{w}{W}$  by 2,  $w$  always being 5 pounds.

On account of the considerable bulk of the sample employed, and the comparatively large weights of powder and mercury that consequently enter into the formula, very close weighing with this instrument is not absolutely requisite. For instance, a variation of 46 grains in the actual value of  $w$  affects the resulting density of the sample by only two points in the third place of decimals. This feature is one of great practical utility, as it enables us to dispense with very small weights, and to abridge considerably the operation of weighing.

**Gravimetric Density of Gunpowder.**—Before the almost universal introduction of breech-loading rifled guns, the gravimetric density of gunpowder was considered to exercise a great influence upon its ballistic value. But even then the importance of this property was greatly overrated, and at present it is of no practical value whatever, except in connection with muzzle-loading guns.

Owing to the terms in which it has been defined, very inaccurate and even erroneous ideas exist as to what is meant by *gravimetric density*.

In the Report of the Chief of Ordnance for 1879, it is defined as "the weight of a given measured quantity," and to this is added: "it is usually expressed by the weight of a cubic foot in ounces."

Major Makinlay, of the Royal Artillery, gives a better idea of what is meant by gravimetric density, but unfortunately confounds it with the air-space of the powder chamber, of which it is approximately a measure. According to the Woolwich Text-book, "the gravimetric density of a charge of powder in the chamber of a gun is the ratio of its weight to the weight of that volume of water which would fill the space behind the projectile in the gun. It is the mean density of the grains of powder and of all the interstitial and other spaces."

It has been further defined as "the weight of a standard volume of the powder, not pressed together except by its own weight." (Ingalls.) None of these definitions appear to me to be satisfactory.

It is hardly necessary to say that the gravimetric density of gunpowder is entirely distinct from its absolute density, or specific gravity; in fact it bears no relation thereto, as will become apparent subsequently, when we shall find that, according to the "gravimeter," an unusually *dense* powder may be made to appear much lighter than a powder of very low specific gravity.

In its general acceptance, the word "density" suggests a comparison, and is almost universally represented by an abstract number, which is the result of a ratio. This is so well known that, except for the errors referred to, the statement would be considered superfluous. I can discover no good reason for discarding the idea, and would therefore define *gravimetric density as the ratio* which the weight of a given volume of the substance, including air and other interstitial spaces, bears to the weight of an equal volume of the standard taken at 15°.5 C. and 760 mm.

As in the case of absolute density there must be a standard to which this ratio is referred. The standard originally adopted in this country, and which is still retained, is the weight in ounces of one cubic foot of distilled water at the standard temperature (assumed to be 1000 ounces).

Since the specifications furnished by the U. S. Ordnance Department for the supply of service powders are expressed in terms of this standard, for practical reasons it will be adopted in our work.

To determine the gravimetric density of any powder, then, it is only necessary to fill the "gravimeter" (a copper measure having a capacity of one cubic foot) and weigh it.

Hence if we represent by  $W'$  the weight in ounces of one cubic foot of the sample, and by  $D'$  the gravimetric density,

$$1000 : W' :: 1 : D' = \frac{W'}{1000}.$$



It is evident that the gravimetric density of the powder would be unity when one cubic foot of it weighed exactly 1000 ounces.

As before stated, from the gravimetric density of a sample of powder an approximately correct idea can be formed as to the volume of air-space in a given charge. The air-space is dependent upon the size and shape of the granules, and the amount of settling and shaking to which the powder is subjected; therefore, in determining the air-space, the percentages are calculated for the powder, both loose and settled.

Knowing the specific gravity, or absolute density, of the powder under examination, as determined by the densimeter, the air-space is found as follows:

Let  $D$  represent the absolute density of the powder;  
 $D'$  the gravimetric density determined as above.

Then  $\frac{D'}{D}$  will be the fractional part, or per cent, of the cubic foot occupied by the powder, and

$1 - \frac{D'}{D}$  the fractional part, or per cent, of the cubic foot occupied by the air, or the *air-space in that volume*.

**The Dupont Gravimetric Balance.**—The apparatus in use at the Artillery School was made by H. Troemner, of Philadelphia, according to designs furnished by Messrs. E. I. Dupont de Nemours & Co., and is used exclusively for the determination of the gravimetric density of small-grained powders such as is used in muskets, mortars, etc. It consists of a small beam-scale resting upon a steel knife-edge, one end of which terminates in a horizontal Y which is also fitted with steel knife-edges (inverted). Suspended from the latter knife-edges by means of steel-faced trunnions is a vase having the shape of a truncated right cone. The vase has a capacity of 4500 grains of distilled water, and can be readily removed from and replaced in the Y during the operation. The other end of the beam is graduated into 100 equal parts, which are marked from 800 to 900 and are read ounces. Along the top

of the beams slides a "rider" by means of which the graduations are read. Immediately below the 900 mark, attached to the under side of the beam, is a small hook, to which may be attached weights, marked 100 and 200 ounces, whenever necessary.

To the extremity of the graduated arm is attached a sliding weight, the use of which will appear later. The graduated arm moves between a slotted standard to which is attached an "arrester" which is manipulated by a milled-head screw. In addition to the weights mentioned, there is a counterpoise, marked 4500, which is required to produce equilibrium in the preliminary operation of adjusting the balance. In addition to the balance proper, a hopper, fitted with a sliding valve, by means of which the gunpowder may be introduced uniformly into the vase during any series of experiments, accompanies the apparatus. The instrument and its appurtenances are contained in a wooden box about  $24'' \times 9'' \times 9''$  to protect it from dust when not in use.

**Precautions to be Observed in the Care and Use of the Dupont Gravimetric Balance.**—1. When not in use, see that the vase is removed from the knife-edges on the Y, and placed in the seat prepared for it in the case.

2. In removing the vase from its seat on the Y, and replacing it, the beam should invariably be arrested, or clamped by turning the milled-head screw to the left. This same precaution should also be observed whenever the counterpoise or weights are placed, the one in the vase or the others on the beam.

3. In producing equilibrium by means of the sliding weight attached to the extremity of the graduated arm, unclamp and approximate by moving the weight by hand; when equipoise is nearly secured, clamp the weight and produce exact equilibrium by means of the smaller weight, which works on the screw-thread projecting from the end of the weight.

4. Equilibrium may be produced in either of two ways; and should there be no occasion for haste, it is well to use one method as a check upon the other.

*First*, place the counterpoise in the vase; attach the smaller (100 oz.) weight to the hook on the under side of the beam and place the "rider" at 800; produce equilibrium by manipulating the sliding weight as just directed.

*Second*, place the counterpoise in the vase; place the "rider" at 900, and proceed as before.

5. Before and after using the instrument, carefully wipe and dust the several parts, including the weights. And before closing the case see that everything is in its proper place.

**The Determination of the Gravimetric Density of Gunpowder with the Dupont Gravimetric Balance.**—Place the vase carefully upon the Y and produce equilibrium as above directed. Then remove the vase, place it upon a large sheet of paper spread upon a table, and place over it the hopper. Fill the hopper with the powder to be examined, open the valve and allow the powder to run into the vase until it is full to overflowing. Close the valve, remove the hopper and "strike" the vase with a straight-edge. Replace the vase carefully upon the Y, and again produce equilibrium by means of the "rider" and weights, if necessary.

From the construction of the apparatus no calculation is required, and it is only necessary to note the readings on the arm and weight, and express the sum decimally.

Thus, suppose that, to reproduce equilibrium when the vase filled with the powder was placed upon the Y, it was necessary to attach the smaller weight (marked 100 oz.) and to place the "rider" at the mark 876 on the arm; the gravimetric density of such a powder would be written immediately 0.976.

**The Gravimeter.**—For determining the gravimetric density of large-grained powders, a copper vessel having the capacity of one cubic foot and called the *gravimeter* is used in connection with the balance already described with the densimeter. Attached to the left arm of the beam-scale of that balance at the point from which the scale-pan is suspended is a hook, the use of which will appear later. The gravimeter



is fitted with handles at the opposite extremities of a diameter and rests upon a cradle, by means of which the powder may be settled without breaking the grains by subjecting them to sudden jars or shocks.

The cradle consists of a stout frame made of oak, about three feet square. Into the parallel upper frame-pieces are set two metal bearings which receive the trunnions attached to the seat upon which the gravimeter is placed. All motion of the seat may be arrested by means of stay-pins. This is necessary whenever it is desired to take the gravimetric density with the powder loose. Uniformity in filling the gravimeter is secured by placing a heavy glass plate across the top of the vessel and noticing whether the granules touch the surface of the glass throughout. The only precautions to be observed in using the gravimeter are those which refer to the balance and have already been enumerated.

**How to Use the Gravimeter.**—First carefully dust the gravimeter within and without, and also the scale-pans of the balance; place the gravimeter on the right-hand pan, and attach the counterpoise to the hook on the left-hand arm. Throw the beam into action, and produce equilibrium, using particles of tin-foil for the purpose if necessary. Having secured equilibrium, throw the beam out of action, remove the gravimeter and place it upon the cradle. Fill the gravimeter loosely, allowing the granules to settle by their own weight, and verifying the full measure by applying the glass plate to the top.

With an assistant replace the gravimeter thus filled upon the balance, and reproduce equilibrium, using for this purpose the weights which accompany the balance. Note the sum of the weights, and divide by 1000; the result will be the gravimetric density of the powder taken *loose*. Throw the beam out of action, remove the gravimeter from the balance and replace it upon the cradle. Withdraw the "stay-pins," and rock the gravimeter until the powder ceases to settle, keeping the vessel filled to the top by introducing additional powder

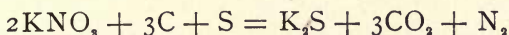


from time to time. Apply the glass plate as before, and when *evenly* full replace the gravimeter upon the balance, and reproduce equilibrium. The sum of these last weights divided by 1000 will be the gravimetric density of the powder taken *settled*.

## LECTURE VIII.

### THE CHEMICAL THEORY OF THE COMBUSTION OF GUN-POWDER.

UNTIL comparatively recent years the equation



was accepted as expressing the chemical theory of the decomposition of gunpowder resulting from its explosion in the bore of a gun. But the results of the investigations of Noble and Abel have shown that this reaction is far too simple, and that, in addition to the few products obtained as represented in the above equation, much more numerous and far more complex products result from the explosion of gunpowder. For instance, the following substances have been found among the *solid products*: potassium carbonate, sulphate, sulphide, hyposulphate, and sulphocyanate, ammonium carbonate, and sometimes free sulphur and carbon; while among the *gaseous products* have appeared carbon monoxide and dioxide, nitrogen, hydrogen, hydrogen sulphide, and marsh-gas.

**Noble and Abel's Calculations.**—This complexity of results led Noble and Abel, after the closest investigation and exhaustive experiments, to the conclusion that "One and the same description of powder, exploded several times in succession, will yield the products of combustion, in the different experiments, in variable proportions; hence the metamorphosis of gunpowder cannot be represented by a chemical equation."

Berthelot differed in opinion from these investigators, and arrived at a different conclusion.



He assumed that the composition of the Waltham Abbey powders was represented as follows:



which requires for 100 parts of powder:

Saltpetre.....	74.8
Carbon.....	13.3
Sulphur.....	11.9

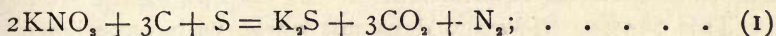
Analysis of these powders gave:

Saltpetre.....	73.55 to 75.04
Carbon.....	10.67 “ 12.12
Sulphur.....	9.93 “ 10.27

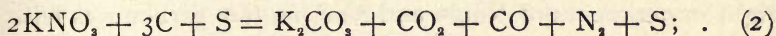
**Berthelot's Theory.**—The following theory was invented by Berthelot to explain the remarkable results of Noble and Abel which led to the still more remarkable conclusion given above. Among the products of explosion enumerated, potassium hyposulphite is not a primary product of the explosion, but is formed during the analysis of the powder residue; while the combined weights of potassium sulphocyanate, ammonium carbonate, hydrogen, and marsh-gas amount to only about 1.5 per cent and, as they originate from secondary reactions, may be neglected. There still remains, however, potassium carbonate, sulphate, sulphide, carbon monoxide and dioxide, the formation of which must be accounted for by any satisfactory theory as to the decomposition of a mixture of saltpetre, carbon, and sulphur.

According to Berthelot's ingenious theory, if we select two from several experiments of Noble and Abel, viz., one in which the maximum amount of potassium carbonate and the minimum of sulphate were produced, and another which yielded the largest quantity of potassium sulphate and the smallest of the carbonate, then the explosion in the first case may be represented by three equations:

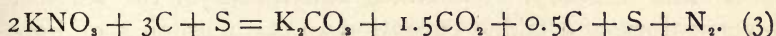
*One third* of the powder would be transformed according to the equation



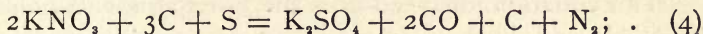
*one half* according to



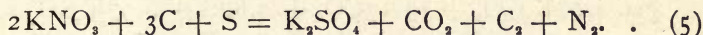
and *one sixth* according to



In the second case, with a maximum of potassium sulphate, *one third* of the powder would be transformed according to equation (1); about *one half* according to equation (3); *one eighth* according to



and *one twelfth* according to



Between the limits marked by these two cases are contained all the experimental results of Noble and Abel. If, therefore, we assume that, in a given experiment, one portion of the powder used burnt according to the equations of the first, and the rest according to those of the second case, the calculated results will agree with those observed. And if the proportions of powder, which are transformed according to the one or other system of equations, be changed from experiment to experiment, the quantities of the products of combustion obtained in each experiment can be calculated in a satisfactory manner.

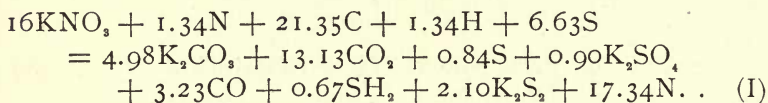
M. Berthelot justifies his assumption that during explosion one portion of the powder is transformed according to one and another portion according to another equation or system of equations, by a further assumption that the local conditions

in a mass of burning powder are not the same in all parts, and that the cooling is too rapid to allow the products to assume a state of chemical equilibrium.

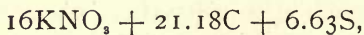
This theory, however, does not agree with experience, since, according to it, considerable amounts of carbon ought to be left free at the end of each explosion, while in twenty-eight experiments of Noble and Abel no free carbon was left, and in only three cases have small insignificant quantities escaped combustion.

**Debus' Theory.**—Discarding the theory of the English investigators, and taking exception to the reasoning of Berthelot, Dr. Debus undertakes to point out the various sources of error in Noble and Abel's methods, and, after applying the necessary corrections, deduces an equation which he claims to represent the metamorphosis of the powders of Waltham Abbey.

This equation, deduced from the 31 experiments published by Noble and Abel, is



The first member of the equation, representing the constituents of the powder, has been calculated from the products of explosion. The same constituents, as found by the direct analysis of the powders, are represented as follows:



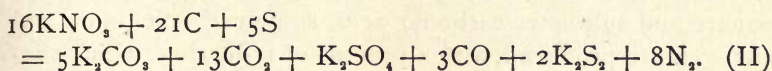
which agree very closely with those deduced from the products of explosion. Powders of this composition, burnt according to the method of Noble and Abel, will form the products of explosion in quantities as represented in equation (I), if the small quantities of secondary products arising from the presence of hydrogen in charcoal, such as marsh-gas, ammonia, and free hydrogen, are neglected.

The sulphuretted hydrogen is either the product of the



direct union of hydrogen and sulphur at comparatively low temperatures, or of the action of carbonic acid and water upon potassium sulphide. In either case its foundation has no direct connection with the explosion, and it ought to be likewise omitted from an equation representing the metamorphosis of gunpowder.

0.84 atom of sulphur is represented as free, because there are no data to show how much sulphur has united with the iron of the apparatus. It is usual to represent the potassium sulphide as monosulphide, while, as a matter of fact, the disulphide is produced. Hence we may substitute for equation (I) a much simpler one, as follows:



(The difference between equations (I) and (II) is due to the union of the sulphur with hydrogen and iron.)

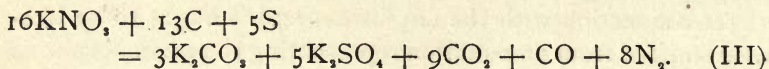
This equation (II) expresses only the quantitative relations between the powder constituents and the products of explosion; the reactions which occur during explosion, which of them are simultaneous, and the order in which they succeed each other have still to be determined.

It may be assumed that, at first, all the potassium of the saltpetre forms with carbon and oxygen potassium carbonate, and that in another stage sulphur acts on the potassium carbonate and produces the mixture known as the solid-powder residue. Or it may be assumed that potassium sulphate is the first product, and that this is afterwards reduced by carbon to potassium bisulphide and carbonate. Both assumptions would lead to the same results.

For an explanation of the formation of potassium sulphate and carbonate, carbonic acid and oxide, and nitrogen, Dr. Debus examines the results of Karolyi's experiments, according to whose investigations these substances formed the chief products of explosion of gunpowder.

The equation deduced to represent the metamorphosis of

the Austrian powders experimented may be written as follows:



From a consideration of these two equations (II and III) Dr. Debus arrives at the first general conclusion as to the decomposition of gunpowder, as follows:

“ The combustion of gunpowder consists of two distinct stages: a process of oxidation, which is finished in a very short time, occupying only a very small fraction of a second, and causing the explosion, and during which potassium carbonate and sulphate, carbonic acid, some carbonic oxide and nitrogen are produced, and a process of reduction, which succeeds the process of oxidation and requires a comparatively long time for its completion.

“ As the oxygen of the saltpetre is not sufficient to oxidize all the carbon to carbonic acid, and all the sulphur to sulphuric acid, a portion of the carbon and a portion of the sulphur are left free at the end of the process of oxidation. The carbon so left free reduces, during the second stage of the combustion, potassic sulphate, and the free sulphur decomposes potassic carbonate. Hydrogen and marsh-gas, which are formed by the action of heat upon charcoal, likewise reduce potassic sulphate, and some hydrogen combines with sulphur, forming sulphuretted hydrogen.”

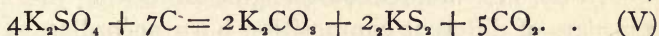
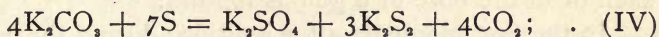
Accepting this view, equation (III) may be assumed to represent the first, and equation (II) the second stage of the combustion of gunpowder. If, moreover, the combustion of ordinary service powder takes place during the first stage according to equation (III), nearly the maximum quantity of heat is obtained which a mixture of saltpetre, sulphur, and carbon can produce.

This equation also corresponds to the most simple relation of the heat of formation of the principal products, and also requires the most simple distribution of the oxygen of the

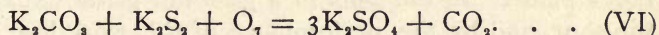
decomposed saltpetre. If the combustion of a mixture of saltpetre, carbon, and sulphur is to produce potassium carbonate and sulphate, carbonic acid, and nitrogen, and if the oxygen of the first three products is to stand to the oxygen of the other in the most simple ratios possible, then the mixture must burn according to an equation the proportions of which so nearly approach those of equation (III) that the latter equation may, without sensible error, be assumed to fulfil all of the foregoing conditions.

The investigator next considers the error arising from assuming that monosulphide of potassium is formed during the combustion of gunpowder, and, from an examination of the results obtained by Berzelius and Mitscherlich, Noble and Abel, and others, shows that, as a matter of fact, potassium disulphide is produced.

From these facts he concludes that the second stage of the combustion of gunpowder takes place according to the equations



The possibility of dissociation requires the additional equation



The final results of the reactions represented by the foregoing equations may be expressed by one equation, as follows:

Let  $x$  represent the number of molecules of saltpetre,

“  $y$       “      “      “      “ atoms      “ carbon,

“  $z$       “      “      “      “      “      “ sulphur,

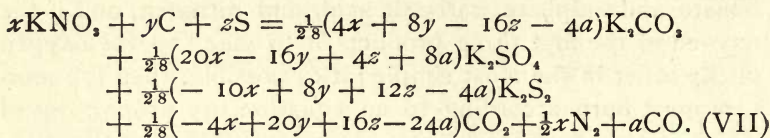
“  $a$       “      “      “      “ molecules of carbonic oxide,

formed by the combustion of such a powder ( $x$ ,  $y$ ,  $z$  being positive numbers).

The general equation representing the qualitative and quantitative relations between the constituents of the powder



on the one hand and the products of *complete* combustion on the other will then be



By means of this equation, we can calculate, from that portion of the powder which produces the chief products, the quantities of these products formed during complete combustion. It would be well just here to classify the products of combustion as follows:

1. Chief products:  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{S}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{N}_2$ .
2. By-products:  $\text{H}_2$ ,  $\text{SH}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{KCNS}$ .
3. Constituents of powder not burnt:  $\text{KNO}_3$ ,  $\text{C}$ , and  $\text{S}$ .

According to what has already been presented, the metamorphosis of gunpowder may be assumed to take place in a shell or in the bore of a gun as follows:

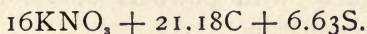
In the first moments after ignition, during the explosion, powders of different composition burn according to equation (III), and in the case of a shell which will burst almost immediately and its contents be scattered about no further change takes place. In the bore of a gun the gases expand, move the shot, and by the performance of this work lose a portion of their energy; the products of the first stage of the metamorphosis, potassic carbonate and sulphate, remain at a red heat, in a fluid condition, for a longer time in contact with free carbon and sulphur, and produce, according to equations (IV) and (V), an additional quantity of carbonic acid.

This carbonic acid, which is generated during the movement of the shot in the bore, prevents the too-rapid diminution of the tension of the gases; the heat of the solid products is, in part, transformed into *vis viva* of the gas-molecules.

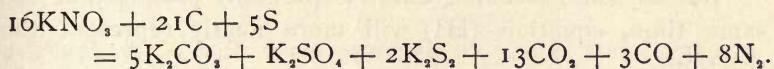
If the gun were long enough and the quantities of carbon and sulphur not too large, every atom of the former might be oxidized by the oxygen of the potassium sulphate, and the

entire amount of the sulphur be converted into potassium disulphide and sulphate by contact with potassium carbonate. But in reality this second stage is never complete; the shot will have left the bore before the termination of these comparatively slow reactions.

**Recapitulation.**—1. The mean composition of the Waltham Abbey powders can be represented as follows:



A. powder of this composition is transformed in Noble and Abel's apparatus according to the equation



The residue of the sulphur, 1.63 atoms, unites partly with hydrogen, partly with the iron of the apparatus.

2. The ordinary service and sporting powders contain for every 16 molecules of saltpetre from 13 to 22 atoms of carbon and from 5.5 to 8.7 atoms of sulphur.

3. A powder composed of *pure* carbon, saltpetre, and sulphur furnishes by its complete combustion potassium carbonate, sulphate, and disulphide, carbonic acid and oxide, and nitrogen as chief products.

4. An increase of pressure appears, *cæteris paribus*, to diminish the amount of carbonic oxide, and in consequence, according to equation (VII), to increase the quantities of potassium carbonate and disulphide, and carbonic acid, and to diminish that of potassium sulphate.

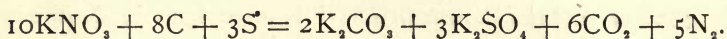
5. The combustion of gunpowder takes place in two stages, one succeeding the other:

(a) A process of oxidation during which potassium sulphate and carbonate, carbonic acid, and nitrogen, and *perhaps* some carbonic oxide, but no potassium disulphide, are produced.

(b) A process of reduction during which carbon and sulphur left free at the end of the first stage react with some of the products formed during that

stage; the free carbon reducing potassium sulphate, with formation of potassium disulphide and carbonate, and carbonic acid; the free sulphur decomposing potassium carbonate with the production of potassium disulphide and sulphate, and carbonic acid. (Equations IV and V.)

6. The first stage of the combustion, the explosion proper, takes place with powders of various compositions according to the equation



But as some carbonic oxide is probably produced at the same time, equation (III) will more nearly represent the reaction.

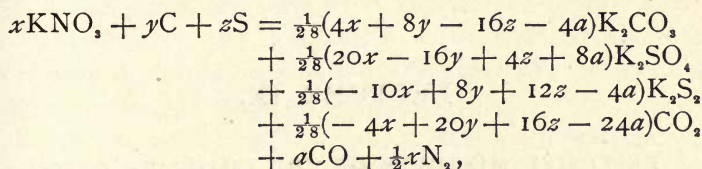
7. In the equation given immediately above, the oxygen in the potassium carbonate stands to the oxygen in the potassium sulphate in the most simple ratios which can exist, if these substances are to be produced by the combustion of a mixture of saltpetre, carbon, and sulphur. In other words, this equation represents the most simple distribution of the oxygen of the decomposed saltpetre among the products of the first stage of combustion. The products as represented by equation (III) are very nearly in the same proportions as in the last equation; therefore it follows that the distribution of the oxygen between potassium carbonate and sulphate, and carbonic acid, according to equation (III), very nearly corresponds to the most simple possible distribution.

8. Ordinary gunpowders contain more carbon and sulphur than is required by equation (III). This excess of carbon and sulphur is left free at the end of the first stage of combustion. The free carbon then acts according to equation (V), and the free sulphur according to equation (IV), and both together form the second stage of combustion. These reactions are endothermic; heat is not evolved, but consumed; they are not of an explosive nature, and in practice are probably seldom complete. The reactions in the second stage increase the volume of the gas formed during the first stage of the



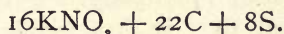
combustion and diminish the temperature of the products. A portion of the carbonic oxide is formed during the second stage by the action of free carbon or potassium disulphide upon carbonic acid.

9. The reactions represented by equations (II), (III), (IV), and (V) can be expressed by one equation, as follows:

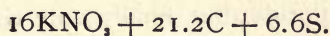


in which  $x$ ,  $y$ , and  $z$  are positive numbers, and represent respectively the number of molecules of saltpetre, the number of atoms of carbon, and the number of atoms of sulphur contained in such a powder; while  $a$  represents the number of molecules of carbonic oxide formed by the combustion of such a weight of the powder.

10. If a mixture of saltpetre, carbon, and sulphur were required which shall possess nearly the greatest energy, and at the same time contain the smallest amounts of carbon and sulphur compatible with this condition, theory would point to the mixture



The service powders of most nations fluctuate about



## LECTURE IX.

### EXPLOSIVE MIXTURES OF THE CHLORATE CLASS.

IN this class of explosive mixtures the chlorates are substituted for the nitrates as oxidizing agents. Berthelot, who discovered potassium chlorate and recognized its oxidizing power, was first to suggest its use in the manufacture of service powders, but his own efforts and the experiments of others in this direction were attended with so numerous and serious accidents that investigations in this direction were temporarily abandoned. The danger attending the manipulation of chlorated mixtures seems to be due to the inherent chemical properties of potassium chlorate, which is the only salt that has been used practically. Potassium chlorate has already been alluded to. It is a friable salt that fuses at  $334^{\circ}\text{C}$ . and decomposes regularly at  $352^{\circ}\text{C}$ ., evolving oxygen and leaving in the first stages of decomposition a mixture of perchlorate and chloride, but finally only the chloride. The decomposition of this salt, unlike most cases of decomposition, is attended with the evolution of heat, liberating, according to Berthelot, at the ordinary temperature, 11 cal. for each equivalent of oxygen (8 gm.) fixed, or 1.4 cal. per gramme of oxygen, or 0.54 cal. per gramme of  $\text{KClO}_3$ . This evolution of heat serves to increase the energy of chlorated explosives, and may be accounted for by assuming that the heat of decomposition of the chlorate is exceeded by that evolved

during the combination of potassium and chlorine to form potassium chloride. This heat, which is liberated at the instant of decomposition, together with the low specific heats of the combustibles, also serves to explain the extreme sensitiveness to shock of the chlorate powders. The reaction also begins at a lower temperature in the case of chlorates than with nitrates, and, on account of the higher temperature at the beginning of the reaction, it is propagated with correspondingly increased rapidity, hence the more energetic and shattering effect of these powders.

Berthelot further explains the effects of chlorate powders on the basis of dissociation, as follows:

“ The compounds formed by the combustion of chlorate powder are all binary compounds, the simplest and most stable of all, such as potassium chloride, carbonic oxide, and sulphurous acid. Such compounds will undergo dissociation at a higher temperature and in a less marked manner than the more complex and advanced combinations, such as potassium sulphate and carbonate, or carbonic acid, which are produced by nitrate powders. It is for this reason that the pressures developed in the first instance will be nearer the theoretical pressures with chlorate than with nitrate powders, and the variation in the pressures produced during the expansion of the gases will be more abrupt, being less checked by the action of the combinations successively reproduced during cooling.”

The explanation, therefore, of the brusqueness and dangerous sensitiveness of chlorate powders may be summed up as follows: The high temperature developed due to the quantity of heat liberated, combined with the relatively low specific heats of the products of combustion; the greater volume of permanent gases, due to the fact that potassium chlorate yields all of its oxygen for the purpose of oxidation, while in case of the nitrate a part of the oxygen is retained by the base;\* and finally the formation of simpler compounds,

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\* This difference in the oxidizing power of these two classes of salts is



involving dissociation in a less marked degree, so that the pressures are more extended in their action.

The danger attending not only the manufacture of chlorate powders, but also to be apprehended in the manipulation and storage of the powders when finished, is so great that the opinions of those who have had to deal with them may be quoted by way of emphasis.

Dr. Duprè, F.R.S., an authority on the subject of explosives, says in this connection: "Chlorate of potassium, on account of the readiness with which it lends itself to the production of powerful explosives, offers a great temptation to inventors of new explosives, and many attempts have been made to put it to practical use, but so far with very limited success. This is chiefly owing to two causes. In the first place chlorate of potassium is a very unstable compound, and is liable to suffer decomposition under a variety of circumstances, and under, comparatively speaking, slight causes,

TABLE SHOWING PERCENTAGE COMPOSITIONS OF NITRATES AND CHLORATES.

	$\text{KNO}_3$	$\text{NaNO}_3$	$\text{NH}_4.\text{NO}_3$	$\text{KClO}_3$	$\text{KClO}_4$
K	38.67	.....	.....	31.89	28.21
Na	.....	27.06	.....	.....	.....
Cl	.....	.....	.....	28.96	25.47
N	13.85	16.46	35.00	.....	.....
H	.....	.....	5.00	.....	.....
O	47.48	56.48	60.00	39.15	46.32

TABLE SHOWING AMOUNT OF AVAILABLE OXYGEN IN NITRATES AND CHLORATES.

	$\text{KNO}_3$	$\text{NaNO}_3$	$\text{NH}_4.\text{NO}_3$	$\text{KClO}_3$	$\text{KClO}_4$
KCl	.....	.....	.....	60.85	53.68
$\text{K}_2\text{O}$	43.03	.....	.....	.....	.....
$\text{Na}_2\text{O}$	.....	36.47	.....	.....	.....
$\text{H}_2\text{O}$	.....	.....	45.0	.....	.....
N	17.41	15.47	35.0	.....	.....
O	39.56	47.06	20.0	39.15	46.32

shown by comparing not so much their percentage compositions as the relative amounts of their *available* oxygen.

chemical and mechanical. All chlorate mixtures are liable to what is termed spontaneous ignition, or explosion in the presence of a variety of materials, more particularly of such as are acid or are liable to generate acid; and all chlorate mixtures are readily exploded by percussion, but more particularly by combined friction and percussion, such as a glancing blow which might easily and would often occur in charging a hole.

In the second place there is some evidence to show that the sensitiveness to percussion and friction increases by keeping, more especially if the explosive is exposed to the action of moist and dry air alternately."

The increased sensitiveness caused by keeping and exposure to moisture is probably due, in part at least, to the chlorate crystallizing out into fine crystals on the surface of the mixture.

Eissler, on the same subject, says: "It is extremely doubtful, from the peculiarities of this salt, if anybody will ever overcome the obstacles due to its inherent chemical properties, which nature manifestly seems to have made unconquerable.

"In mixing these compositions great danger is attendant, and too much circumspection cannot be used. They explode instantly on any violent stroke, very often by friction alone; sometimes spontaneously, as when in a state of rest, and no known cause for their combustion can be ascertained.

"Many are deluded as to its safety by so-called experiments with freshly made powder. Manufacturers of this compound may attempt to show its safety by hammering and cutting it and similar tests; but let the powder be exposed to the natural atmospheric action, attract some moisture during a damp foggy night, then get dry, and the least friction or blow will cause an unexpected explosion."

To this Major Cundill, R.A., H. M.'s Inspector of Explosives, adds: "Without going so far as to say that it is impossible to manufacture a safe chlorate mixture, it is a fact that out of many which have been examined with a view to their introduction into this country, not one has yet been

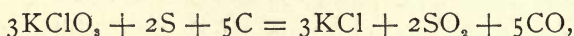
found to be safe enough to be licensed, with the exception of asphaline. . . .

“ I do not pretend to say that powerful and valuable explosives may not be, and have not been, manufactured with chlorate of potash as their main ingredient, but I contend that, though these are fairly safe when used for special purposes and by experts, none have as yet been brought to notice (with the previously named exception) which are suitable for general use by the mining population, and which could be relied upon not to cause accidents under ordinary conditions of transport, storage, and use.”

The explosives resulting from the use of the chlorates may, broadly speaking, be divided into two classes, those in which no particular attempt is made to diminish the dangerous sensibility of the chlorate mixtures, and those in which, by the addition of some diluting ingredient or by some special mechanical treatment, endeavors are made to diminish this sensibility.

According to Berthelot, a powder in which the nitre is replaced by an equivalent quantity of chlorate should have a heat of combustion greater by one half than that of the gunpowder, and should possess double the force.

The reaction resulting from such a substitution may be represented as follows:



which corresponds fairly well to a powder having the composition of

KClO <sub>3</sub> .....	75.00 parts
S.....	12.50 “
C.....	12.50 “

Besides the erosion of the walls of the gun by the chlorate powders, the chlorine sometimes liberated after firing is deleterious to those exposed to its action.

These disadvantages, together with those already enu-



merated, are not compensated for by the superior explosive power of the mixtures.

Several chlorate mixtures, however, have been proposed and patented, some of which are given.

**Asphaline.**—This substance consists of thoroughly cleansed wheat or barley bran impregnated with potassium chlorate mixed with potassium nitrate and sulphate. Paraffine oil, paraffine, ozokerite, and soap, or some of these substances may be added. The mixture in commerce is colored pink with fuchsine.

The proportions of the several ingredients are:

Potassium chlorate.....	54	parts
Bran .....	42	“
Potassium nitrate, }	4	“
Potassium sulphate }		

In reporting upon this powder, H. M.'s Inspectors of Explosives in their Report for 1890 note that two samples of asphaline were examined which had been kept in store for a number of years. One of the two was quite mouldy. Nevertheless both samples were in good condition as far as their safety was concerned, and they gave little or no indication of increased sensitiveness to friction or percussion such as is often noticed in chlorate mixtures.

**Melland's Paper Powder.**—The following mixture is boiled for an hour in 79 parts of water:

Potassium chlorate.....	9.00	parts
“ nitrate ... ..	4.50	“
“ ferrocyanide.....	3.25	“
“ chromate .....	0.06	“
Charcoal .....	3.25	“
Starch .....	0.05	“

Strips of porous paper are then dipped into the liquor, rolled into the form of cartridges, and dried at 100° C. To prevent their absorbing moisture they are given a coating with

a solution formed by dissolving one part of xyloidine in three parts of acetic acid (sp. gr. 1.04). This paper is cheap, easy to make, and fairly safe. It does not give off much smoke or leave much residue, nor does it erode the piece in which it is fired, while it is more powerful than gunpowder.

**Augendre's Powder.** — This is also known as White German or American Powder, and consists of

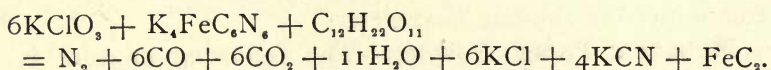
Potassium chlorate.....	50 parts
“ ferrocyanide .....	25 “
Cane-sugar.....	25 “

The substances are moistened and mixed in bronzed mortars and granulated.

Pohl, who submitted this powder to many trials, modified the composition as follows:

Potassium chlorate. ....	49 parts
“ ferrocyanide.....	28 “
Cane-sugar.. ....	23 “

Being in the proportion of three equivalents of the chlorate to one of each of the others. Pohl represented the products of combustion of such a powder as follows:



From his calculation 100 grammes of the powder give 52.56 gm. of solid products and 47.44 gm. of gas, which has a volume at 0° and 76 cm. of 40,680 c.c., and at the temperature of combustion (valued at 2604°.5 C.) a volume of 431,162 c.c. These conclusions are all in favor of the white powder, but they have never been verified.

Sixty parts by weight, or 77.4 by volume, are equivalent to 100 parts of gunpowder, and they give but 31.35 parts of solid residue, where 100 parts of gunpowder, according to Bunsen and Schischkoff, give 68 parts. Besides, the temperature of the resulting gas is not so high for the white

powder, and hence a greater number of shots may be fired without heating the piece excessively. The ratio of the temperatures is as 0.779 to 1. But the estimation of the temperature is based on the hypothesis held as to the nature of the reaction, and on the calculated temperature of the reaction, neither of which has been demonstrated exactly.

If the process goes on precisely as Pohl believes, it is difficult to explain the erosive action of this powder upon guns from which it is fired.

Augendre and Pohl claimed other advantages for this powder, viz., it keeps perfectly in free air, inflames easily on contact with a spark, can be employed without being granulated, is simple to manufacture, and is inexpensive.

According to Pohl, the manipulation of this powder presents absolutely no danger if the substances are pure and contain neither sulphur nor carbon, and they cannot be exploded by a blow of iron on iron or by friction.

Experience does not confirm these assertions. Several instances of explosion are known to have taken place when the materials were mixed with great care; and a bottle filled with the powder has exploded when exposed to the sun in summer. Even if the undoubted dangers which exist in the use of white powder were overcome, still the erosive action which it exerts on the gun would tend to proscribe it for this use. The erosive action of the powder is most marked on cast-iron and steel guns, and it has therefore been proposed to limit its use to bronze guns and to the charging of shells, for which it seems especially appropriate. According to Hudson, glass bulbs filled with concentrated sulphuric acid are placed in the shells with white powder, and the shock of impact, when the shells strike the object to be destroyed, is sufficient to break the bulb, liberating the acid, which upon coming into contact with the powder ignites it and causes explosion.

**Dynamogen.**—M. Pétry has devised the following process for manufacturing an explosive paper, which he calls *dynamogen*.



He dissolves yellow prussiate of potash in pure water, and heats the solution until it boils, when he adds powdered charcoal, stirring the mixture well. Allowing this to cool, he next adds successively potash, chlorate of potash, and starch, triturated in water.

The proportions are as follows:

Potassium ferrocyanide .....	17 parts
Water.....	150 “
Charcoal.....	17 “

boiled, well stirred, and allowed to cool; to which are added

Potash .....	35 parts
Potassium chlorate.....	70 “
Starch .....	10 “
Water.....	50 “

The whole mixture is made into a thin paste, and spread with a brush on ordinary filtering-paper. The paper is dried on a moderately heated plate, and as soon as one side is thoroughly dry the other side is varnished in a similar manner. Three coats are given each side, and the paper so impregnated is cut up and rolled into cartridges.

**Hahn's Powder** consists of

Potassium chlorate .....	367.5 parts
Antimony tersulphide.....	168.3 “
Spermaceti.....	46.0 “
Charcoal .....	18.0 “

The last three substances are thoroughly mixed, and the chlorate added just before the powder is to be used, the mixing being done by sieves. The addition of the spermaceti is claimed to protect the mixture against explosion by friction.

**Horsley's Powder** consists of a mixture of finely powdered potassium chlorate and gall-nuts in the proportions of three to one.

The powder may be granulated by passing it through a

sieve while in a damp state. The ungranulated form of powder experimented with in Austria for use in small arms was not satisfactory. The granulated powder is stated to explode at  $221^{\circ}\text{C.}$ , and its *force* to be five times that of gunpowder.

**Pertuiset's Powder** is recommended for use mainly as a *detonating* powder, or for filling bullets or shells. It has, in the past, been used in the manufacture of explosive bullets. It consists of

Potassium chlorate.....	2.000	parts
Sulphur.....	1.000	"
Sporting gunpowder.....	0.125	"
Animal charcoal.....	0.020	"

**Parone's Explosive** consists of two parts of potassium chlorate and one of carbon disulphide.

From experiments in Italy with the 9-cm. and 15-cm. projectiles it was concluded that this mixture was an exceedingly safe one; that it would not explode without a fuse—not always a desirable quality—and that, although its effects were not strikingly superior to those of gunpowder, they increased rapidly with an increase of calibre.

**Petrofracteur**, a chlorate powder recently endorsed by the Austrian military committee, consists of

Potassium chlorate.....	67	parts
Nitrobenzene. ....	10	"
Potassium nitrate.....	20	"
Antimony sulphide.....	3	"

As in the case of the nitrates, so with the chlorates, the list of proposed mixtures is well-nigh unlimited. By far the majority of these powders have proven worse than useless, for reasons already given. *Those mixtures intended for use as fuse compositions are the only ones that have become of any practical value.*

**Fuse Compositions.**—Of the vast number of chlorate

powders proposed, only those mixtures intended for use as fuse compositions have proven of general value in practice.

**Davey's Fuse Composition**, which consists of

Potassium chlorate.....	6 or 6 parts
“ nitrate.....	5 “ 3 “
“ ferrocyanide.....	2 “ 4 “
“ bichromate.....	5 “ — “
Antimony sulphide.....	5 “ 3 “

**Hill's Fuse Compositions**, which were prepared by Mr. Hill while chemist to the U. S. Naval Torpedo Corps, and were designed for the several systems of torpedoes.

**Fuse Composition for the Contact System.**—This system requires a composition more sensitive than that used in either the percussion-cap or cannon primer.

The following mixture proved satisfactory, and is made by finely powdering and mixing together, under alcohol:

Potassium chlorate.....	60.50 parts
Antimonious sulphide.....	33.50 “
Phosphorus (amorphous)....	6.00 “

**Composition for Friction Fuses.**—Satisfactory results were obtained when the following mixture was used to explode spar torpedoes:

Potassium chlorate.. .....	44.44 parts
Manganic oxide.....	44.45 “
Phosphorus (amorphous)....	11.11 “

The ingredients must be finely powdered separately, mixed under alcohol, and used while wet.

**The Sulphuric-acid Fuse.**—This belongs to a class of fuses known as chemical fuses. The substances are separated and kept apart until required for action, when they are brought into contact, and unite chemically with the evolution of heat and production of flame. Such action occurs when



sulphuric acid is brought into contact with a mixture of equal parts of potassium chlorate and cane-sugar. When these materials only are used the action of the fuse is somewhat sluggish, particularly when the fuse has been manufactured for any length of time. But if the following ingredients, in the proportions given, be used, the ignition will be instantaneous:

Potassium chlorate.....	41.4 parts
“ ferrocyaniide. ....	17.2 “
Cane-sugar .....	41.4 “

**Composition Used in the Harvey Fuse.**—The principle of this fuse is precisely the same as that just described. The sulphuric acid reacts upon the following mixture:

Potassium chlorate.....	17.0 parts
Cane-sugar.....	4.5 “
Nut-galls.....	1.5 “

**Composition for Fuses to be Exploded by Frictional Electricity.**—The following mixture is used in all igniters made at the U. S. Naval Torpedo Station for use with frictional machines:

Potassium chlorate.....	45.00 parts
Antimonious sulphide.....	20.75 “
Phosphorus (amorphous)....	5.75 “
Carbon.....	28.50 “

The ingredients are finely powdered separately, mixed under alcohol, and used while wet.

**English Priming Material** originally consisted of

Copper subphosphide.....	10 parts
“ subsulphide. ....	45 “
Potassium chlorate .....	45 “

The proportions of the ingredients are now varied, in order to produce compositions of different degrees of sensitiveness. The ingredients are prepared and mixed as described above.

**Austrian Priming Material** consists of

Potassium chlorate.....	I part
Antimony sulphide.....	I "
Plumbago (powdered).....	trace

## LECTURE X.

### CLASSIFICATION OF EXPLOSIVE COMPOUNDS. EXPLOSIVE COMPOUNDS OF THE NITRO-SUBSTITUTION CLASS.

THE explosive substances thus far treated of have been produced by mixing together mechanically combustible substances with oxidizing salts. We shall now consider that class of explosives known as *explosive compounds*, in which the oxidizing agent is introduced chemically into the molecule, thus forming no longer a mixture but a true chemical compound, each molecule of which contains the oxidizing atoms and atoms having a strong affinity for oxygen. It is evident that the relation existing between the constituents in the latter case must be far more intimate than in the former.

As has been already stated, the chief *explosive compounds* are formed by the action of nitric acid upon various organic substances containing carbon, hydrogen, and oxygen. This combination of the oxides of nitrogen with the hydrocarbon groups may give rise to two *classes* of explosive compounds, viz:

*Nitro-derivatives of the Aromatic Series of Hydrocarbons, or Nitro-substitution Compounds, and*

*Nitric-derivatives from Alcohols, or Nitric Ethers and Esters.*

**Nitro-substitution Compounds.**—This class of substances, most of which are themselves explosive, or enter as important ingredients into a large class of explosives, differ from nitric



ethers in that they cannot be decomposed by distinct reactions so as to reproduce the original substances which combine to form them.

The principal organic substances so far used in connection with explosives of this class are the hydrocarbons of the aromatic series.

As a rule, the aromatic compounds are richer in carbon than the fatty compounds, containing at least six carbon atoms, and when decomposed by various methods yield as one of the products *benzene*. They not infrequently appear as products of vegetable life, but more frequently they are obtained from coal-tar by fractional distillation.

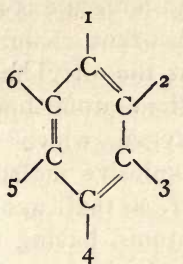
When treated with alkalies nitric acid is not reproduced, but various nitrogenous substances are formed, and when subjected to the action of reducing agents the result is the formation of amides.

As a class the nitro-compounds are less energetic in their action and more stable than the nitric ethers.

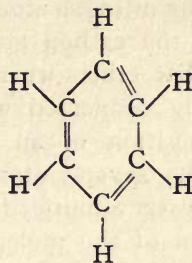
This is explained by Berthelot by the application of the principles of thermochemistry, the loss of energy involved in the formation of this class of explosives being considerably greater than that entailed by the formation of the nitric ethers.

Thus in the case of nitrobenzene potash, which when combined with dilute nitric acid liberates only 13.7 Cal., cannot supply by a simple reaction the energy requisite to reproduce the acid and benzene, the union of which, in order to form nitrobenzene, liberates 36.5 Cal. In the case of nitric ether and nitroglycerine, however, only from 4 to 6 Cal. are necessary to reproduce each equivalent of acid, so that the requisite energy is available for the regeneration of the original substances. The difference in the molecular structure of these two classes of explosives may further serve to explain in part the greater intensity of action of the nitric ethers as compared with nitro-compounds.

Thus the carbon chain of aromatic hydrocarbons and the benzene ring may be represented as follows:



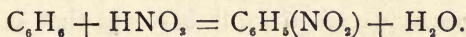
Six-carbon Ring.



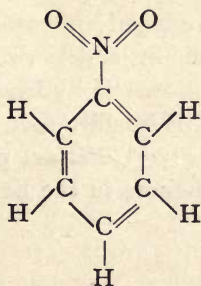
Benzene Ring.

In acting upon any member of the aromatic series of hydrocarbons with nitric acid in order to form a nitro-substitution compound, one or more atoms of hydrogen are replaced by one or more molecules of the univalent radical nityl ( $\text{NO}_2$ ), and in this transfer the nitrogen atom of the nityl radical is attached directly to the carbon atoms.

Thus, by acting upon benzene with nitric acid to form nitrobenzene, the reaction may be represented as follows:



In the formation of nitrobenzene one atom of hydrogen in the benzene has been displaced, and one molecule of the univalent radical nityl ( $\text{NO}_2$ ) has been substituted therefor. This transfer may be shown in the structural formula for benzene, thus:

Nitrobenzene— $\text{C}_6\text{H}_5\text{NO}_2$ .

in which the nitrogen atom of the nitryl molecule is connected *directly* to the carbon atom of the benzene chain. In the case of nitric ethers we shall see that the nitryl molecule is not directly connected with the carbon atom, but through the interposition of an atom of oxygen, which serves to separate the several atoms of the explosive molecule having the greater affinities for each other, so that, upon the decomposition of the molecule, these atoms, having a greater distance to traverse before they can combine, acquire a correspondingly increased momentum, thereby causing greater interatomic activity and energy, which results in correspondingly increased intensity of action.

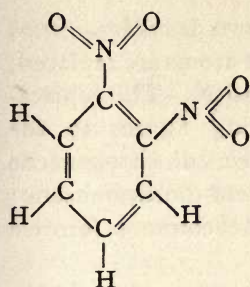
It is readily seen that when only one atom of hydrogen is replaced in the benzene chain, the resulting product must be the same irrespective of which particular atom is replaced (since they all bear the same relation to the carbon atoms to which they are attached), or by what method the change is accomplished.

This, however, is not the case when two or more atoms of hydrogen are replaced, since it is found that such multiple replacement gives rise to the formation of isomeric compounds, which, in the case of explosives as in other products, possess characteristic properties, and it is not a violent assumption to suppose that the stability of the explosive molecule may depend largely upon the relative positions of the atoms replaced by the nitryl radical in the aromatic chain.

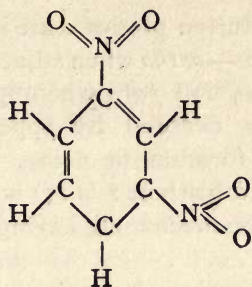
Thus, by acting upon mono-nitrobenzene with concentrated nitric acid, a more highly nitrated product is obtained, namely, di-nitrobenzene, in which two molecules of nitryl are substituted for two atoms of hydrogen.

Upon inspection it is readily seen that there are three (and only three) separate and distinct positions that the substituted molecules can assume in the benzene ring, thus:

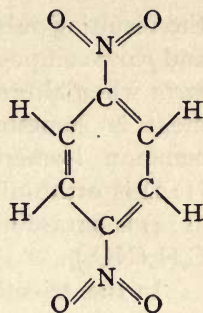




(1)

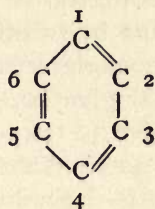


(2)



(3)

For purposes of explanation we may orient the ring, beginning at the uppermost carbon atom, and, proceeding around to right, designate each atom by means of a number, thus:



Although there is but one molecular formula for di-nitrobenzene —  $C_6H_4(NO_2)_2$  — there may be three structural or graphic representations of this compound as indicated above, and if the theory of molecular structure be true, each of these compounds should possess certain characteristic properties. In support of this theory note the three isomeric compounds formed by substituting two molecules of hydroxyl (OH) for two atoms of hydrogen with the formation of dioxy-benzene. If in the substitution of OH for H, in the ring, two adjacent atoms of H (1 and 2, etc.) be replaced, the result is *pyrocatechin*; if alternate atoms (1 and 3, etc.) be replaced, the result is *resorcin*; and, finally, if opposite atoms in the ring be replaced (1 and 4, etc.), we have *hydroquinone*.

According to the relative positions of the replaced atoms,

the resulting substitution products are known as *ortho*-, *meta*-, and *para*-compounds—*ortho* when adjacent atoms are replaced, *meta* when alternate, and *para* when opposite. The replacement is sometimes denoted by appending figures to the common isomeric formula or name, thus: di-nitrobenzene (1:2) is *ortho*-dinitrobenzene; (1:3) is *meta*-dinitrobenzene; (1:4) is *para*-dinitrobenzene, all having the common formula  $C_6H_4(NO_2)_2$ .

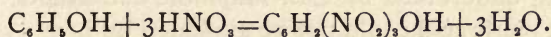
In the tri-substitution derivatives the same principle obtains. There may be three (and no more) compounds formed by replacing three atoms of H, and if the replacement be by the same radical, the resulting substitution products will be isomeric, and, according to the positions of the replaced hydrogen atoms, they are distinguished as *adjacent* (1:2:3), *symmetrical* (1:3:5), and *asymmetrical* (1:2:4).

The number of isomer-derivatives depends entirely upon the replacing radicals; thus by substituting the same radical there can be but three isomeric tetra-substitution products; two dissimilar radicals may give 20, three such radicals may give 16, while four may give 30 tetra-derivatives.

Although it cannot be asserted absolutely that the stability of the explosive molecule is dependent upon or regulated by the position of the replaced atoms in the ring, there is much evidence to show that it is at least affected thereby, and, other things being equal, the symmetrical substitution-derivative is the most stable, as might be expected, since, by the arrangement of its atoms, it would naturally require a greater disturbance to destroy the equilibrium of the molecule. We shall have occasion to refer to this subject again in connection with the nitric derivatives, nitric ethers and esters.

**Tri-nitro-phenol, or Picric Acid.**—One of the best examples of this class of explosive compounds is Tri-nitro-phenol, or *Picric Acid*, which was discovered by Hausmann in 1788. He made it by treating indigo with nitric acid. It may be obtained in various ways, but the cheapest and best source is from the action of nitric acid on phenol, or “*carbolic acid*,” one of the products of the distillation of coal-tar.

The reaction may be represented by the following equation:



It may be prepared experimentally by introducing into a glass flask of 150-c.c. capacity about 5–10 c.c. of fuming nitric acid, and adding cautiously, in very small quantities, about 1–2 c.c. of carbolic acid. The reaction is very violent, and is attended with the copious development of nitrous fumes. When the reaction has subsided and the flask become cold, yellow crystals of picric acid will be found in the liquid.

Picric acid is made commercially by melting carbolic acid and mixing it with strong sulphuric acid, then diluting the "sulpho-carbolic" acid with water, and afterwards running it slowly into a stone tank containing nitric acid. This is allowed to cool, when the crude picric acid crystallizes out, the acid liquid (which contains practically no picric acid, but only sulphuric with some nitric acid) being poured down the drains.

The crude picric acid, after being drained, is transferred to the "boiling-stones," where it is dissolved in water by the aid of steam and afterwards allowed to cool, when most of the picric acid recrystallizes.

The "mother-liquor" is then transferred to the precipitating-tank, in which the picric acid still left in solution is precipitated by the addition of sulphuric acid.

The picric acid left in the "boiling-stones" is once more dissolved in hot water, and this second solution is transferred to the crystallizing-tank, where it is left to cool, and where the picric acid again crystallizes. Finally, the picric acid, after draining in the tank, is transferred to a centrifugal machine to remove the excess of moisture, and then dried on glazed earthenware trays in a steam-box in which the temperature is not allowed to exceed 100° F. According to Hill and Abel, picric acid does not explode, but when heated it burns quickly and sharply with a bright flame.



An investigation into the subject of the explosiveness of picric acid, undertaken by Col. Majendie and others, tends to show that picric acid could not be exploded by heat even when confined in large masses, but it was by no means proven that it could not, under certain circumstances, be exploded by the action of fire.

Desortiaux states that when heated *slowly* it vaporizes without undergoing any decomposition, but when heated *brusquely* to a temperature a little above 300° it explodes with violence.

Berthelot has also recently studied this subject, and confirms the view of Desortiaux. He says: "Should a nitro-compound, such as picric acid, while burning in large masses, happen to heat the sides of the containing enclosure to a degree sufficient to induce deflagration, the deflagration might combine to further increase the temperature of the enclosure, and the phenomenon might, occasionally, be transferred into a detonation. It would even suffice that the detonation should occur in an isolated point, either during a fire, or owing to the local overheating of a boiler or apparatus, to enable it to originate the explosive wave and propagate itself by influence throughout the whole mass, causing a general explosion."

There exists no doubt, however, that picric acid is liable to be exploded by detonation or by a blow, and that the picrates and the mixtures of picric acid, with oxidizing agents, are highly explosive.

In 1873 Sprengel stated that "picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxidizers, a powerful explosive when fired with a detonator. Its explosion is almost unaccompanied by smoke."

Apart from the investigation above referred to, the detonation of picric acid has recently attracted attention from the alleged use of this substance by the French Government in a particular fused and consolidated condition, as an explosive, under the name of *mélinite*.

M. Eugene Turpin has also taken out a patent which

claims the employment "as an explosive agent for military or other uses of the tri-nitro-phenol, or picric acid, of commerce, unmixed with any oxidizing substance," by the use of a powerful fulminate detonator, or by the use of an intermediate priming of picric acid in powder, primed by the fulminate, or by dispensing with the fulminate and employing a sufficiently large charge of ordinary quick-burning powder enclosed in a strong tube and made to burst inside the charge of picric acid.

The explosiveness of picric acid by detonation has been investigated experimentally, with the following results:

1st. Dry picric acid may be perfectly detonated by means of a 5-grain fulminate detonator.

2d. The detonation of a small quantity of dry picric acid is capable of detonating a quantity of picric acid placed at a short distance from it.

3d. The detonation of picric acid containing, at any rate, as much as 17 per cent of water may be effected by detonating a charge of dry picric acid.

4th. A thin layer of cold picric acid will be exploded by a weight of 54 pounds falling 20 feet, and *it may be exploded* by one pound falling 26 inches. The sensitiveness greatly increases with warming, so that when heated to a temperature just below its melting-point (about 240° F.) a weight of one pound falling 14 inches will explode it.

**Borlinetto's Powder.**—As far back as 1867 Borlinetto proposed a mixture of picric acid and other oxidizing agents for blasting purposes. The ingredients and the proportions in which they were to be mixed are as follows:

Picric acid.....	10.0 parts
Sodium nitrate .....	10.0 "
Potassium chromate.....	8.5 "

The resulting powder proved too sensitive to be of practical value.

Many salts, known as *picrates*, have been derived from picric acid, but the only ones which have been used to any ex-

tent for explosive purposes are the salts of potassium and ammonium. All of the picrates, except  $C_6H_2(NO_2)_3ONH_4$ , are readily exploded by heat or blows.

**Potassium Picrate** ( $C_6H_2(NO_2)_3OK$ ).—This is one of the most violently explosive of the picrates. It is made by mixing warm potassium carbonate with a boiling solution of picric acid in water. On cooling, the liquid deposits small crystalline needles of a golden-yellow color which show green and red colors by reflected light. Heated gradually to  $310^\circ C$ . it explodes violently; and it may also be detonated by a sharp blow.

When mixed with oxidizing agents, and especially potassium chlorate, its explosive properties are very much increased. Such a mixture approaches very nearly to nitroglycerine and guncotton in violence, but it is so sensitive to friction and shocks as to be practically useless. When containing 15 per cent of moisture, potassium picrate is safe from detonation by blows, and ignites only locally on contact of flame.

Several mixtures containing the potassium salt have been experimented with, but with no great degree of success.

**Fontaine's Powder**, consisting of potassium picrate and chlorate, was made and tested in Paris as a charge for shells and torpedoes, but it was very dangerous to manipulate, and, after a terrible accident in 1869, it was abandoned.

**Designolle's Powder**.—This powder is made on a large scale at Le Bouchet in France, and is graded according to the proportions of the ingredients, which are potassium picrate and nitrate, with or without the addition of charcoal.

The compositions of the four varieties made at this factory are as follows:

Designolle's Powder.	Torpedoes and Shells.		Cannon.			Small Arms, Muskets, etc.	
			Ordinary Calibre.		Large Calibre		
Potassium picrate.....	55	50	16.4	9.6	9 0	28.6	22.9
Potassium nitrate.....	45	50	74.4	79.7	80.0	65.0	69.4
Charcoal.....	.....	.....	9.2	10.7	11.0	6.4	7.7



These powders were made according to the ordinary processes followed in the manufacture of gunpowder, from 6 to 14 per cent of water being used, and the trituration being three hours for torpedo-powder, six hours for musket-, and nine hours for cannon-powder. The powder was granulated as usual. The torpedo- and shell-powders were tried at Brest and Toulon with excellent results. According to Roux and Sarrau, the heat of combustion of the 55 per cent. mixture will be 916 cal., and of the 50 per cent. 1180 cal.

The cannon- and musket-powders were noted for their uniformity of action, the variations in the initial velocities of the projectiles being not more than two metres. According to Jouglet, 60 grammes of Designolle powder produced the same result as 350 grammes of ordinary powder, while the force of these mixtures could be varied between quite wide limits, according to the amount of picrate which they contained. In spite of their superior ballistic properties, Designolle powders appear to be less brisant than black powder. They give scarcely any fumes while burning, and do not erode the piece in which they are fired.

The picrates constitute a series of crystalline bodies of definite composition and known reactions, and there is no reason to apprehend that they may decompose "spontaneously."

**Ammonium Picrate** ( $C_6H_2(NO_2)_3ONH_4$ ) is prepared by saturating warm picric acid with concentrated ammonia-water. When neutralization is complete another charge of picric acid is dissolved in the same liquid and ammonia again added. The solution is allowed to stand and cool, when the salt crystallizes out in transparent orange-colored prisms. It may also be obtained crystallized in beautiful citron-yellow needles by treating picric acid with ammonium carbonate. According to Hill and Abel, if flame is applied to ammonium carbonate, it burns without any tendency to explosion. It is almost insensitive to blows or friction. According to Desortiaux, it explodes when heated to about  $310^\circ C.$ , but if heated in free air to a temperature below  $300^\circ C.$  it fuses and burns.

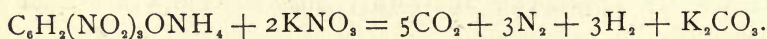
**Brugère Powder.**—This powder has been made to some extent in France, and has been found to be stable, safe to manufacture and handle, but rather expensive. It consists of

Ammonium picrate.....	54 parts
Potassium nitrate ... ..	46 “

Heated to  $310^{\circ}$  C. this mixture burns with one half the velocity of ordinary powder. Its force is about twice or three times that of black powder. It is but slightly hygroscopic, leaves but little residue (which is not erosive), and gives off a small amount of inodorous gas. Experiments with the chassépot showed that 2.6 grammes of this powder produced the same effect as  $5\frac{1}{2}$  grammes of regulation powder.

Brugère powder is said to give a velocity of more than 2000 feet per second with small arms, and to cause very slight recoil. Large numbers of cartridges of this powder were ordered for the new Lebel rifles, but it is stated that a recent examination of a quantity of this ammunition that had been stored at Chalons showed that the powder had deteriorated to such an extent that the whole lot had to be condemned.

Brugère expresses the reaction produced by the explosion as follows:



Hence 100 grammes of the powder should give 69.14 grammes of gaseous products, which at  $0^{\circ}$  and 76 cm. would have a volume of 52.05 litres. A direct determination gave 48 litres. Compared with the analogous results obtained by Bunsen and Schischkoff for black powder, the ratio of the volumes is as 2.5 : 1. It is extremely doubtful, however, whether a reaction (as above given) will yield  $\text{CO}_2$  and H at the same time.

**Abel's Powder.**—About the same time that Brugère introduced his powder, Abel patented a similar powder in England which consisted of a mixture of ammonium picrate, potassium nitrate, and charcoal. When flame is applied to particles of this mixture they deflagrate with a hissing sound,

but the deflagration has but little tendency to spread to the contiguous particles; but if the mixture be strongly confined, as in shells, it explodes violently, and exerts a destructive action, less powerful than that of guncotton, nitroglycerine preparations, and Designolle powder, but considerably greater than that of gunpowder. It is to be remarked that while ammonium picrate and potassium nitrate mixed in these proportions undergo mutual decomposition, with the production of the highly deliquescent salt, ammonium nitrate, yet if the two be *dissolved* together in water, the addition of sufficient water to even thoroughly moisten the mixture appears to induce no such change, since when again dried the mixture seems to have no greater tendency to absorb moisture from the air. Indeed the powder is no more hygroscopic than black powder, and appears to be fully as stable, while the fact that water may be used in incorporating the ingredients without any detriment to the final product renders its manufacture, at least, not more dangerous than that of ordinary gunpowder, and it may be subjected to the same processes of pressing and granulating as are applied to the latter.

Shells charged with picric powder have been fired in England from guns of different calibres up to the 9-inch gun, with a charge of 43 pounds of R. L. G. powder, and without an accident of any kind. Some comparative experiments have also been instituted between this powder and compressed guncotton in submarine mines, the results of which indicated that the destructive action of the two was not very different when applied under the pressure of water. For use in large submarine mines *wet* guncotton is undoubtedly more efficient, but for use in small offensive torpedoes the granular form of the picric powder can be used to great advantage in completely filling the case.

Professor Hill made Abel's powder as follows:

Ammonium picrate.....	42.18 parts
Potassium nitrate.....	53.97 “
Charcoal (best alder).....	3.85 “

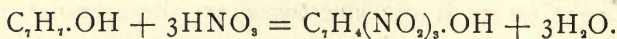


These ingredients were moistened with water and worked under wheels, granulated, etc., as in the manufacture of ordinary powder. Thus obtained the powder had a yellowish-green color, was easily granulated, and no difficulty was experienced in working it.

Compared with gunpowder as to the amount required as a bursting-charge for cast-iron spherical shells, the force of this powder was found to be to that of gunpowder as 1.75 to 1. It appeared, however, to burn imperfectly, giving off a heavy greenish-yellow smoke, which was supposed to be due to imperfect working of the mixture under the wheels, and to too small a proportion of  $\text{KNO}_3$ , as is evident from an examination of the proportions used.

As a charge for fuses and igniters excellent results were obtained. As may be inferred from what has already been said, nitro-substitution compounds may be derived from almost every substance rich in carbon and hydrogen, but as yet very few such compounds have become prominent except those derived from benzole, naphthaline, etc., which are now being largely used as important constituents of such explosives as bellite, securite, roburite, etc.

**Tri-nitro-cresol.**—Tri-nitro-cresol is similar to tri-nitro-phenol, or picric acid, and may be obtained from cresol precisely as picric acid is derived from phenol, or carbonic acid; that is, by treating it with nitric acid and substituting for three atoms of hydrogen three molecules of nitryl ( $\text{NO}_2$ ), with the formation of the nitro-product, and three molecules of water, thus:



The formation of isomeric compounds, all of which are represented by the same formula— $\text{C}_7\text{H}_4(\text{NO}_2)_3.\text{OH}$ —during the process of nitration, will be referred to later.

Tri-nitro-cresol crystallizes in yellow needles which are slightly soluble in cold water, but rather more so in boiling water, alcohol, and ether. It melts at about  $100^\circ \text{C}$ .

In France, tri-nitro-cresol is known as "*Cresilite*," and, mixed with mélinite, is used for charging shells.

By neutralizing by means of concentrated ammonium hydrate ( $\text{NH}_4\text{OH}$ ) a boiling-hot saturated solution of tri-nitro-cresol, a double salt of ammonium and nitro-cresol crystallizes out upon cooling which is similar to ammonium picrate. This salt is known as "*Ecrasite*," and has been experimented with in Austria for charging shells. Ecrasite is a bright yellow solid, greasy to the touch, melts at  $100^\circ \text{C.}$ , is unaffected by moisture, heat or cold, ignites when brought into contact with an incandescent body or open flame, burning harmlessly away unless strongly confined, and is insensitive to friction or concussion. It is claimed to possess double the strength of ordinary dynamite, and requires a special detonator (containing not less than 2 gm. of fulminate) to provoke its full force. Notwithstanding the excellent properties attributed to this explosive, several imperfectly explained and unexpected explosions that have occurred in loading shells with it have prevented its general adoption up to the present time.

**Mélinite.**—For many years the secret of the composition of this explosive was so well guarded that nothing definite could be learned about either the character of the ingredients or the method of manufacture. At present, however, there seems little doubt as to the composition of the original mélinite, although the French claim that the original invention has been so modified and perfected that the mélinite of to-day cannot be recognized in the earlier product.

As originally invented, mélinite consisted of a mixture of fused picric acid and tri-nitro-cellulose dissolved in a mixture of ether and alcohol. Theoretically the following proportions were required, and the process of incorporation is as follows:

Dissolve

Guncotton..... 30 parts

in a mixture of

Ether.....	2 parts	} 45 parts
Alcohol.....	1 part	

and to this add

Picric acid (fused and pulverized) 70 parts

The ether-alcohol mixture is allowed to evaporate spontaneously and the resulting cake is granulated.

In place of the ether-alcohol mixture, acetone, which is equally efficacious and less expensive, may be used.

Mélinite possesses the characteristic yellow color of picric acid, has a bitter taste, is almost without crystalline appearance, and when ignited by a flame or heated wire it burns with a reddish-yellow flame, giving off copious volumes of black smoke.

The earlier forms of mélinite were very unstable, several explosions resulting both from handling and during manufacture, notably that in the factory at St. Omer, France, which destroyed six adjacent factories and two houses. Within the last two years, however, the French claim to have so far perfected the original explosive that it is now a perfectly safe explosive in manufacture, handling, transportation, and storage, but one accident having occurred from its use within three years. Its present composition is not definitely known, but it is generally believed to contain picric acid mixed with some oxidizing substance. Its use alone in shells has been discontinued, and, instead of mélinite alone, about two thirds of the space within the shell is filled with *cresilite*. The remaining space—one third—is then filled with mélinite, which is rammed in by means of mallets.

It is claimed that no mélinite shell has ever burst in a gun, and no accident has ever occurred in drawing the charges from the shells. France is reported to have a full supply of mélinite shells ready for use ashore and afloat.

There seems to be but little doubt that the English explosive "*Lyddite*" is identical with the original mélinite, the secret having been purchased by the English Government from M. Turpin, the inventor of mélinite.

**Mono-nitrobenzene, or Nitrobenzene.**—This nitro-com-



pound has already been referred to, and in the same connection the principle upon which it is made.

It was discovered by Mitscherlich in 1834, and is now manufactured on a very large scale for use in the preparation of aniline. According to the strength of the acids used, the resulting compound will be mono-, di-, or tri-nitrobenzene.

In order to obtain the mono-nitro-compound, 40 parts of  $\text{HNO}_3$  of specific gravity 1.400 is mixed with 60 parts of  $\text{H}_2\text{SO}_4$  of specific gravity 1.840, and to every *three* parts of this mixture *one* part of pure benzene is added. The proportion of  $\text{H}_2\text{SO}_4$  may be reduced to  $58\frac{2}{3}$  per cent, that of  $\text{HNO}_3$  being raised to  $41\frac{1}{3}$  per cent. On account of the violence of the reaction the benzene should be added gradually to the acid mixture, and also, on account of the volatility of both the benzene and the nitro-product, the temperature during the process of manufacture should be kept as low as possible. This can be accomplished generally by means of a current of water and, when made in the laboratory, by agitating the flask from time to time. When the reaction is complete, the nitrobenzene will appear upon the surface of the acid mixture, and may be separated by drawing off the acids by means either of a siphon or of a separatory funnel. To avoid the formation of any of the di-nitro-product, an excess of benzene may be added, which will be subsequently found mixed with the nitro-product, whence it may be separated by fractional distillation, its boiling-point being considerably lower. After separation from the acids it is thoroughly washed, first in water, and finally in a weak alkaline solution, in order to free it from all traces of acidity.

Nitrobenzene varies in color from being practically colorless to a deep reddish orange; it is oily in appearance, boils between  $205^\circ$  and  $210^\circ$  C., solidifies at  $3^\circ$  C., and at  $15^\circ$  C. has a specific gravity of 1.187. It possesses the strong characteristic odor of "bitter-almond oil," a sweet burning taste, and is poisonous in both gaseous and liquid state. It is but slightly soluble in water, but dissolves readily in alcohol, benzene, and concentrated nitric acid. In the cold it dis-

solves nitrocellulose, reducing it to a pasty or jelly-like consistency. In commerce it is largely known as "Mirbane Oil."

Nitrobenzene is not in itself an explosive under ordinary circumstances, but when highly heated it decomposes with the evolution of nitrous fumes, and if thrown in small quantities upon an iron plate or into an iron vessel at a red heat it detonates violently. Ignited it burns with a reddish, smoky flame. Its value as an explosive is derived from mixing it with high explosives, such as guncotton, nitroglycerine, etc., where it acts as a *deterrent*, either retarding or preventing explosion. When mixed in small quantities with nitroglycerine it has been found to lower the freezing-point of that explosive. When mixed with potassium chlorate it forms one of the principal ingredients of "Rack-a-rock" (this explosive will be considered later).

**Di-nitro-benzene.**—By acting upon benzene with the strongest acids obtainable, nitric and sulphuric, and allowing the temperature during reaction to rise to  $100^{\circ}$  C., two atoms of hydrogen will be replaced by two nitryl molecules (of the  $\text{HNO}_2$ ) with the formation of the di-nitro-compound.

On the manufacturing scale, however, di-nitrobenzene is prepared by renitrating the mono-nitro-compound. This method may be reproduced in the laboratory as follows:

Prepare an acid mixture consisting of 40 parts of nitric acid (sp. gr. 1.500) and 60 parts of sulphuric acid (sp. gr. 1.845) and, without waiting for this mixture to cool, to every two parts add one part of mono-nitrobenzene. During the reaction the temperature will reach  $100^{\circ}$  C., and copious nitrous fumes will be evolved which should be either condensed, or discharged in the open air by means of a hood or other contrivance. After the reaction ceases, the contents of the flask should be brought gradually to a state of gentle ebullition, and kept at that temperature for ten or fifteen minutes, and then allowed to cool. The contents of the flask should next be decanted upon a filter, and the solid residue,

which generally consists of a mixture of ortho-, meta-, and para-di-nitrobenzene, washed upon the filter until all traces of acidity disappear.

Thus prepared, di-nitrobenzene is a hard, crystalline solid, the crystals being long brilliant prisms, varying in color from a light lemon-yellow to about the color of ordinary brown sugar. As already stated, the formula  $C_6H_4(NO_2)_2$  represents three isomeric compounds, of which the *meta*-derivative is most abundantly produced by the method just described, and may be distinguished from the other isomers by its melting-point; the *meta*-derivative melting between  $83^\circ$  and  $89^\circ$  C., the *ortho*- at  $118^\circ$  C., and the *para*- at  $172^\circ$  C.

Properly made, di-nitrobenzene should contain no traces of the mono-compound, and should be odorless. It is soluble in warm water and alcohol, and, like the mono-compound, is poisonous.

It is not of itself explosive, and when heat is applied to it fuses, and gradually becomes ignited, burning with a smoky flame. When mixed with substances rich in oxygen, and especially when the oxygen is held in feeble combination, it forms strong explosives, e.g., bellite, securite, etc.

**Tri-nitrobenzene.**—The tri-nitro-derivative of benzene may be prepared by treating meta-di-nitrobenzene with a mixture of concentrated nitric and Nordhausen sulphuric acids. It may also be made by decomposing tri-nitrobenzoic acid— $C_6H_3(NO_2)_3CO_2H$ —into carbonic acid and tri-nitrobenzene by heating it to  $210^\circ$  C., its melting-point.

Tri-nitrobenzene has not been used as an explosive or ingredient of explosives until very recently, and consequently very little is known of its properties as such. It has been proposed as a substitute for picric acid in powders containing that ingredient, but it is weaker than picric acid, and beyond that its power and properties remain to be developed.

**Bellite** is a Swedish explosive which was discovered by Carl Lamm, of the Rötbro Explosive Manufactory, Limited, near Stockholm, and consists of a mixture of ammonium



nitrate and meta-di-nitrobenzene in the following proportions:

Ammonium nitrate.....	5 parts
Meta-di-nitrobenzene.....	1 “

These ingredients are heated up to 80° or 90° C. (the melting-point), and, when in a melted condition, are mixed with saltpetre, forming a true explosive compound. When pressed warm and granulated it has a specific gravity of from 1.2 to 1.4, and a gravimetric density of from .800 to .875.

Heated in an open vessel bellite loses its consistency at 90° C., but does not begin to separate below 200° C.; at that point evaporation begins, and increases with a higher temperature, without explosion, however. Suddenly heated bellite burns with a sooty flame, but upon the removal of the source of heat it ceases to burn and assumes a caramel-like structure, the ingredients being the same as in its original state with the exception of a smaller proportion of saltpetre. After it has been pressed bellite is not especially hygroscopic; if pressed while hot, the subsequent increase of weight does not exceed 2 per cent.

During February 1889 an experimental exhibition of the properties of bellite was given at Chadwell Heath, England, and the following tests were made in the presence of a large number of visitors:

1. A charge of  $1\frac{1}{2}$  pounds of the explosive was placed in a can and fired under water. The can being water-tight, this experiment might have been omitted.

2. A 4-ounce charge of bellite—which somewhat resembled a stick of sulphur—was broken in two, and one end thrown into a coal fire, where it melted and burned quietly. The other end of the stick was placed upon a  $\frac{3}{8}$ -inch iron plate and exploded by means of a detonator. The plate was bulged. This experiment illustrated the fact that while bellite cannot be exploded by ordinary combustion, yet when detonated by proper means it exerts a powerful force.

3. A mass of iron weighing 120 pounds was dropped from

a height of about 16 feet upon 5 charges of bellite placed on an iron plate. The explosive was ground to pieces without explosion.

4. Five ounces of this crushed bellite were placed in a can and detonated in contact with a steel-faced iron rail, the rail being fractured by the force of the explosion.

5. A quantity of bellite was mixed with 1 pound of blasting-powder and buried in a hole 3 feet deep. This charge was fired by a plain powder fuse, but the bellite, although blackened and burned somewhat on its surface, was thrown about unexploded.

6. A charge of bellite was fired like a bullet from a small arm against a  $\frac{3}{8}$ -inch iron plate. Pieces of the explosive were found adhering to the plate unexploded.

7. The ballistic properties of bellite were illustrated by firing from a mortar a 32-pound shot, first with a charge of  $\frac{1}{2}$  pound of powder, and then with  $\frac{1}{4}$  pound of bellite. In the first case the range attained was  $40\frac{1}{2}$  yards; in the latter 95 yards.

8. Its explosive effect was next compared with that of dynamite under similar conditions. Four ounces of each explosive were placed upon  $\frac{3}{8}$ -inch iron plates, covered with moist clay, and detonated. The effects were about the same, although it was claimed that the explosive effect of bellite was more widely distributed than that of dynamite.

9. It was next tried to explode bellite in mines by means of ordinary powder fuses. In all cases the bellite failed to explode, while gunpowder was readily exploded under similar circumstances.

10. A charge of 8 pounds of bellite was placed in a mine 3 feet deep beneath a length of railway line laid in chairs fixed in cross-sleepers with fishes, etc., complete, and exploded by means of a detonating fuse. The entire structure for many feet was thrown in the air, the rails being broken in one place and bent in others, fishes broken, etc.; while the sleepers were torn and split, one chair broken, and a crater about 12 feet in diameter opened.

Some of its other properties, such as its freedom from flame, the harmless nature claimed for its products of combustion, etc., were not tested.

In connection with these experiments the claims of the inventor are given. M. Lamm claims for bellite the following advantages:

1. That it is one of the most powerful explosives known, being stronger than guncotton, gunpowder, or dynamite.

2. That it possesses qualities of safety entirely foreign to explosive substances generally, as follows: It presents no danger whatever in manufacture; it cannot be made to explode by friction, shock, or pressure; it cannot be made to explode by fire, lightning, or electricity; it can only be made to explode by means of a detonating cap, and is therefore absolutely safe.

3. That upon being exploded no noxious gases are given off, and therefore it is particularly adapted to blasting in mines, etc.

4. That bellite, made expressly for coal or rock blasting, does not shatter like dynamite, but detaches the material in large blocks with but a small percentage of dust.

5. That it does not undergo any chemical change from time nor atmospheric influences, always retaining its non-explosive character until the fulminating cap is applied to it.

6. That it can be used in shells that would prove of a terribly destructive character, and that such shells may be fired from guns of large calibre with the service charge of powder without risk to the piece.

7. That bellite can be safely manufactured in tropical climates, and transported by land or sea as ordinary merchandise.

8. That it requires no thawing, as it does not freeze or change its character in even the coldest weather.

9. Finally, that it can be profitably manufactured and sold at a lower price than dynamite or any other explosive possessing equal force.

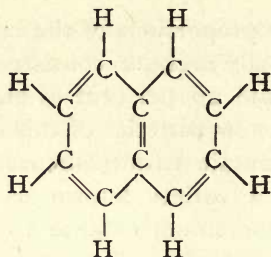
**Securite.**—This explosive is almost identical with bellite,



differing only in the proportions of the ingredients when first introduced. Originally securite consisted of 74 per cent of ammonium nitrate and 26 per cent of meta-di-nitrobenzene. Recently, however, new varieties of this explosive have been introduced, which contain tri-nitro-benzene, and di- and tri-nitrobenzene; also a variety known as *Flameless Securite*, made by adding ammonium oxalate to the varieties mentioned. Securite is a bright-yellow granular substance which is said to be non-hygroscopic, and capable of being kept for any length of time without undergoing any change. It is insensitive to friction and percussion, cannot be exploded by a flame or incandescent body, requiring a detonating cap to provoke an explosion. Its strength is said to be equal to that of dynamite No. 1.

**Nitro-toluene.**—Similar nitro-compounds may be derived from toluene as have been enumerated under benzene, but only one such derivative, namely, di-nitro-toluene, has as yet been found of practical value in its application to explosives. In preparing di-nitro-toluene it has been found most advantageous to use the strongest acids (nitric and sulphuric) and to treat toluene directly, rather than prepare the mono-compound and re-nitrate that product. As in the case of benzene three isomeric compounds are produced. Dinitro-toluene is a solid crystalline body, the crystals having the form of slender needles; it melts at about  $71^{\circ}\text{C}$ . is soluble in boiling water and alcohol, and decomposes at temperatures above  $300^{\circ}\text{C}$ . It is not itself explosive, but lends itself readily to the formation of various grades of explosives when mixed with other explosive substances. It has recently attracted attention on account of its use in the manufacture of smokeless powders.

**Mono-nitronaphthalene.**—Like benzene, naphthalene, when treated with nitric acid, gives rise to a large class of nitro-compounds, many of which have been experimented with in making explosives. The formula for naphthalene is  $\text{C}_{10}\text{H}_8$ , and the molecular arrangement of the atoms may be represented graphically as follows:



As in the case of benzene, this formula serves to explain the great number of isomeric substitution-products.

Mono-nitronaphthalene may be made by introducing finely pulverized naphthalene into a mixture consisting of four parts of nitric acid (sp. gr. 1.400) and five parts of sulphuric acid (sp. gr. 1.840), taking care that the temperature does not fall below  $160^{\circ}$  F. so as to prevent solidification of the nitro-compound during the process of conversion. When the reaction is complete, the entire contents of the flask (or other vessel) are decanted and allowed to cool, and the nitronaphthalene solidifies. The solid mass is then removed, melted with hot water, and thoroughly washed with constant agitation until free from all traces of acidity. A better method of preparing this substance is to dissolve the naphthalene in glacial acetic acid and add to the solution nitric acid (sp. gr. 1.420), in the proportion of four parts of  $\text{HNO}_3$  to every one part of naphthalene dissolved. As soon as all of the nitric acid has been added the entire contents of the vessel are brought to gentle ebullition, and this temperature maintained for fifteen minutes. Upon cooling the mono-nitro-naphthalene is deposited in long, slender, yellow prismatic needles. It melts at about  $61^{\circ}$  C., is only slightly volatile when heated, is insoluble in water, but readily dissolves in alcohol, benzene, carbon bisulphide, and is decomposed when heated above  $300^{\circ}$  C.

Although not itself explosive, mixed with other substances it is used in the manufacture of a large class of explosives.

**Di-, Tri-, and Tetra-nitronaphthalene.**—The di-derivative of naphthalene may be made by dissolving naphthalene

in boiling nitric acid (sp. gr. 1.500), or by treating mono-nitronaphthalene with nitric acid (sp. gr. 1.52) in the cold, or by treating naphthalene at a temperature of about 70°C. with a mixture of one part of concentrated nitric acid and two parts of sulphuric acid.

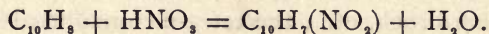
By boiling di-nitronaphthalene with fuming nitric acid tri-nitronaphthalene is formed, and by subjecting the same derivative to the prolonged action of boiling nitric acid (fuming) it is converted into tetra-nitronaphthalene. These various nitronaphthalenes are separated from the acids and purified as described in the preparation of the mono-nitro derivative.

Di-nitronaphthalene forms brilliant yellowish crystals, which when heated gradually melt at about 185° C., but if subjected suddenly to high temperatures deflagrate. It is sparingly soluble in alcohol, ether, carbon bisulphide, and cold nitric acid, but dissolves readily in benzene, acetic acid, and turpentine.

Tri-nitronaphthalene crystallizes out in yellowish tabular crystals, and the tetra-nitro-compound in prisms of the same color, both of which explode when heated. All of the nitronaphthalenes have been experimented with in connection with explosives, and combined with other substances form powders which have been patented in Belgium under the name of *Favier Powders*. These powders are also known in England as *Ammonites*, and in other countries as *Nitramites*.

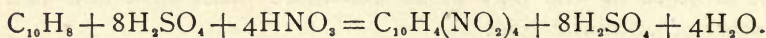
**Volney's Powders.**—In view of the attention which nitro-substitution compounds are receiving at present, it may be of interest to note the letters patent granted Mr. C. W. Volney in 1874.

His invention consists in mixing *nitrated naphthalene* with an oxidizing agent. By acting upon naphthalene with nitric acid of varying strength, substances are produced of corresponding degrees of nitration. Thus with nitric acid having the specific gravity of 1.40 the mono-nitronaphthalene is produced:





While by using a mixture of strong sulphuric acid (sp. gr. 1.845) and nitric acid having a specific gravity of 1.50 we obtain the tetra-nitronaphthalene:



All of the nitronaphthalenes will form explosive compounds when mixed with oxidizing agents which can supply sufficient oxygen to oxidize the surplus carbon; and it is evident that the higher the degree of nitration of the naphthalene, the less of the oxidizing agent will be required, while at the same time the greater will be the breaking power of the explosive.

Thus in order to make an explosive of moderate breaking power, which is therefore better adapted to military purposes, or blasting in soft and fissured rock, etc., the mono-nitronaphthalene is used, being prepared commercially by incorporating

Naphthalene.....	100 pounds
Nitric acid (sp. gr. 1.40).....	400 “

and leaving these substances in contact for four or five days, at the end of which time the naphthalene has been converted into a brown crystalline mass, which is thoroughly washed with water, dried and pulverized. This the inventor calls “Nitrated Naphthalene No. II.”

The explosive made from this product is formed by mixing thoroughly

Nitrated naphthalene No. II.....	1.00 pound
Saltpetre.....	3.30 “
Sulphur.....	0.51 “

These substances can be pulverized and mixed in the same manner as in the manufacture of ordinary gunpowder.

To prepare an explosive of great breaking power, such as would be adapted to filling torpedoes, submarine blasting, blasting of hard rock, etc., the tetra-nitronaphthalene is used,

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which, prepared as follows, is called "Nitrated Naphthalene No. I." Commercially this nitro-compound is made by treating naphthalene with a mixture of two parts of strong nitrosulphuric acid (sp. gr. 1.845) and one part of nitric acid (sp. gr. 1.50) at a temperature of 100° C., in the proportion of

Napthalene.....	100 pounds
Nitrosulphuric acid .....	400 "

At the end of one hour the reaction is finished, all of the naphthalene having been converted into a bright yellow crystalline mass, which is washed, dried, and pulverized as already indicated.

A very powerful explosive is made from this nitro-substitution product, as follows:

Nitrated Napthalene No. I. ....	2.18 pounds
Saltpetre .....	0.19 "
Sulphur .....	0.16 "

In both of these powders any other nitrate or any chlorate may be substituted for saltpetre.

These powders are of a yellow color, and are unusually insensitive to friction, percussion, concussion, and heat, and are therefore safely handled, stored, and transported. When unconfined except in the form of cartridges, they ignite and burn away harmlessly. It requires a powerful detonator, or a priming of guncotton, nitroglycerine, or dynamite, to develop their full power. Experiments in the Artillery School laboratory show the relative strength of powders Nos. I and II to be respectively 58.44 and 53.18, as compared with standard nitroglycerine.

**Favier Explosives.**—In his investigations looking to a reduction of the inherent dangers of nitroglycerine, M. Favier concluded that it was possible to make an explosive in which the nitrogen and carbon elements were simply placed in juxtaposition, but not combined. Acting upon this conclusion he patented certain mixtures, which are known in Belgium as *Favier Powders*, but in England they are called *Ammonites*, and in other countries *Nitramites*.

According to his patents, M. Favier seeks "to replace explosive nitrogen compounds, like fulmicotton and nitroglycerine, in which the nitrogen compound and hydrocarbon elements are united in one definite compound, by simple mixtures of these same elements." He further proposes to use in the fabrication of his new powders substances which under ordinary conditions are absolutely stable, but which by greatly increasing the initial detonation, either by increasing the charge of fulminate in ordinary blasting-caps, or by using an initial priming of guncotton or dynamite, could be fully detonated. These principles were applied in Belgium in 1887 to a mixture having the following composition:

Ammonium nitrate.....	75 parts
Resin .....	5 "
Charcoal.....	20 "

The mixture was forcibly compressed into a hollow cylinder, and the interior of this cylinder was filled with dynamite, which formed the initial detonator. It was found that, while a fulminate cap alone would not explode the compressed mixture, if the mixture were granulated it could be detonated by 2 grammes of fulminate.

In his more recent powders M. Favier has materially changed the compositions. The enveloping cartridge is made of ammonium nitrate and nitronaphthalene "in the proportions necessary to produce a gas at the moment of oxidation." These proportions are approximately as follows:

Ammonium nitrate.....	90 parts
Nitronaphthalene.....	10 "

The nitronaphthalene is melted and poured around the ammonium nitrate, which is thus enclosed for protection on account of its hygroscopic properties. Briefly described, the process of manufacture is as follows:

The nitrate is thoroughly dried by passing it slowly upon an Archimedean screw through a trough warmed by steam, and is then pressed into a warmed former and sprinkled with



melted nitronaphthalene. In this manner a homogeneous roll is formed which passes next to the graining-machine. When granulated the grains are sifted, the smaller particles being reserved for intermediary detonators to be placed in the cartridge-core, while the larger grains are moulded warm into hollow cartridges, which are subsequently covered with paraffin, and after the detonator is inserted the whole is enveloped in paraffin paper.

In France the government has secured control of these powders, and in the factory at Saint-Denis five varieties are made:

I.	Grisounite—Ammonium nitrate.....	95.5	parts
	Tri-nitronaphthalene.....	4.5	“
II.	Grisounite—Ammonium nitrate.....	92.0	“
	Di-nitronaphthalene.....	8.0	“
III.	Poudre Favier, No. 1—Ammonium nitrate..	87.5	“
	Di-nitronaphthalene.	12.5	“
IV.	“ “ No. 2—Ammonium nitrate..	44.0	“
	Sodium nitrate.....	40.0	“
	Di-nitronaphthalene.	16.0	“
V.	“ “ No. 3—Sodium nitrate.....	75.0	“
	Mono-nitronaphthalene. ....	25.0	“

The ingredients used in these powders being very stable substances, they can be manipulated with great security, and their transport presents no danger. It is claimed for them that they are insensible to shock, fire, and cold; in fact their excess of stability is their only fault, as it requires one gramme of the fulminate of mercury to provoke detonation. On the other hand, the hygroscopic nature of ammonium nitrate, which forms so large a proportion of these powders, requires great precaution in storage.

Of the varieties given above, Poudre No. 3 seems to give the best results.

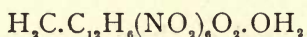
**Emmensite.**—In January 1888 letters patent were granted to Dr. Stephen H. Emmens, of New York, for a new organic

acid discovered by him, to which the name of *Emmens Acid* has been given, and the compounds formed with this acid bear the general name of Emmensite.

According to Dr. Emmens, the discovery of the so-called Emmens Acid, or EACID, was purely accidental, and resulted from a mixture of picric and nitric acids, the latter of "exceptionally high specific gravity," which had been gently warmed and set aside for some weeks, at the end of which period the new acid had crystallized out. The existence of the new acid has been questioned, and Emmens Acid, or Eacid, has been considered by several eminent chemists merely an isomeric form of picric acid. According to an analysis by Dr. Wurtz, the relative percentage compositions of eacid and picric acid are as follows:

	Eacid.	Picric Acid.
Carbon.....	31.84	31.44
Hydrogen.....	2.04	1.31
Nitrogen.....	17.14	18.34
Oxygen.....	48.98	49.91
	<hr/> 100.00	<hr/> 100.00

Dr. Wurtz assigned to this acid the formula



and regarded it as intermediate between tri-nitro-phenol and tri-nitrocrosol. Professor Remsen, of the Johns Hopkins University, declared the new acid to be merely a very pure form of picric acid, while Lieut. John P. Wisser, of the First U. S. Artillery, assistant professor of chemistry at the U. S. Military Academy, after carefully examining the new acid, stated that it was "simply picric acid which has mechanically absorbed, probably in crystallizing, the fumes of nitric acid or the acid itself." On the other hand, the inventor, Dr. Emmens, and Dr. Wurtz, of Pittsburgh, have maintained that the newly discovered acid is not *identical* with pure picric acid. Emmens acid has been obtained in the Artillery School laboratory by dissolving picric acid at a gentle heat in fuming

nitric acid (sp. gr. 1.500 to 1.550) and evaporating the solution to about two thirds of the original volume. Upon cooling, the new acid crystalizes out in long, transparent crystals, varying in form from prismatic to rhomboidal. In color it also differs from picric acid, possessing a greenish-yellow rather than straw yellow color; it is also less soluble in water and alcohol, and melts at a lower temperature, evolving brownish-red fumes and undergoing change of color. All of these points of difference, however, may be explained by the theory of Lieut. Wisser as to the composition of the new acid.

In the specifications of the letters patent granted on March 4, 1890, Dr. Emmens describes the methods of preparing emmensite substantially as follows:

“The materials I employ are such hydrocarbon substitution-derivatives as are capable of fusion by heat without decomposition, and are also capable, when fused, of dissolving the nitrates of soda, potash, ammonia, which are the preferred oxidants. The most suitable hydrocarbons for the purpose, so far as I have discovered, are the tri-nitrophenols, tri-nitro-cresols, and (if the working temperatures do not exceed 120° C.) the new acid patented to me January 10, 1888.

“The conditions under which the new type of explosives is produced consist in the employment of a sufficient degree of heat and in continuing this heat until actual liquefaction of the mixture is attained. The manner in which I carry out my new process of manufacturing explosives is as follows: I take two open vessels, both heated, by steam-jackets or by any other convenient method, to the same temperature. In one of these I place the tri-nitrophenol, and in the other I place the nitrate of soda or other oxidant in a finely pulverized and dried condition. When the combustible is entirely fused I add thereto the heated oxidant in small quantities at a time, and I stir the mixture thoroughly. I then gently raise the heat until the oxidant becomes fully liquefied, or so combined with the combustible as to form a semi-fluid homogeneous mass. The mixture is then removed from the vessel and allowed to cool for use.”

By varying the proportions of the several ingredients, as



well as the ingredients themselves, an infinite number of explosives may be obtained, all of which would belong to the class of emmensites.

Practically the inventor recommends three grades, as follows:

No. 35, to be used for blasting purposes, consisting of picric acid and sodium and ammonium nitrates; No. 259, for military and naval use, shell and torpedo charges, etc., consisting of picric acid, di-nitrobenzene, and sodium and ammonium nitrates; and No. 5, as a substitute for gunpowder, consisting of picric acid, sodium nitrate, and charcoal or flour.

These grades have been made upon a small scale in the Artillery School laboratory and subjected to various tests as to strength, stability, etc. As the result of the earlier experiments (made over five years ago), the claims for stability and great explosive force made for this explosive were not verified, and with the conviction that the investigation had been most impartially and carefully conducted, those results were incorporated in the former edition of these lectures, as well as in the pamphlet prepared for the instruction of artillery gunners. Subsequent experiments by myself, and particularly investigations by the Naval Bureau of Ordnance, as well as by the Board of Ordnance and Fortifications of the Army, have convinced me that it is possible to make emmensite which, when loaded in shells, torpedoes, or other receptacles that may be closed tightly so as to protect it from atmospheric changes (and especially exclude moisture), will preserve its stability and explosive force for years. Exposed to damp air, however, emmensite quickly absorbs moisture and develops acidity. Such samples as have been experimented with have either been carefully prepared from chemically pure materials, or have been procured from commercial sources, although I would have preferred to experiment with samples direct from the factory, and endeavored to secure such samples several times. As the result of the investigations referred to (by the military and naval authorities), it has been

shown that emmensite when freshly made, or when protected from dampness, possesses great explosive force, and moreover may be safely fired as shell charges from high-powered rifled ordnance, although it would seem from these experiments that there is a limit to the amount that can be thus fired.

The importance of this last property overshadows all other claims yet made for this explosive, especially since it has also been demonstrated that shells charged with emmensite do not require special fuses, but that an explosion of a high order may be developed by means of a simple fuse which may be ignited by an ordinary percussion-cap.

**Gelbite.**—Gelbite is but another form of emmensite, and was patented by the inventor of that explosive. According to letters patent, it is “an explosive substance, consisting of paper, or paper-stock, converted into a nitro-compound and impregnated with ammonia and picric acid.”

It may be prepared as follows: Sheets of paper, of convenient size, are immersed in a mixture of nitric and sulphuric acids (in proportions of 1 to 3) for about three minutes, and are then removed and washed, first with water, and then with a solution of ammonium carbonate. It is then steeped in a hot solution of picric acid and allowed to remain until thoroughly saturated, the result being a sheet of nitrocellulose impregnated with picric acid, ammonium picrate, nitrate, and sulphate, the proportions of which vary according to the treatment. Thus prepared gelbite has the appearance of a sheet of yellow paper. Ignited it burns quickly, with but little smoke; the fumes, however, possess all the disagreeable features of picric acid. It has been proposed to use gelbite as a propellant in small arms, but experiments in that direction have not justified its adoption.

**Roburite.**—This explosive was invented by Dr. Carl Roth, a German chemist, and, according to the license authorizing its manufacture in Great Britain, it consists of

“(a) Nitrate of ammonium with or without an admixture of nitrate of sodium and neutral sulphate of ammonium, or either of them, provided that the amount of nitrate of sodium

shall in no case exceed 50 per cent of the total amount of nitrates present, and

“(b) Thoroughly purified chlorinated di-nitrobenzole with or without the addition of thoroughly purified chloronitronaphthalene and chloro-nitrobenzole; provided (1) that such chlorinated di-nitrobenzole shall not contain more than four (4) parts by weight of chlorine to every one hundred (100) parts by weight of chlorinated di-nitrobenzole; and (2) that the proportions of chloro-nitronaphthalene and chloro-nitrobenzole shall not amount to more than 2 per cent and 5 per cent respectively of the finished explosive.”

In addition to these ingredients nitronaphthalene is also sometimes used. In introducing chlorine into the nitro-compound, Dr. Roth claims to have greatly increased the dynamic effect of the explosive, the formula for chloro-di-nitrobenzole being  $C_6H_3Cl(NO_2)_2$ , and the percentages of nitrogen and chlorine being therefore respectively 13.82 and 17.53. Roburite is made by first thoroughly drying and pulverizing the ammonium nitrate, which is then heated in a closed steam-jacketed vessel to  $80^\circ C$ . The chloro-di-nitrobenzole is melted and added to the heated ammonium salt and the ingredients thoroughly incorporated by constant stirring.

Thus made, roburite is a yellowish-brown powder, possessing the characteristic odor of nitrobenzole (bitter almonds) and having a specific gravity of 1.40. It burns quickly, but cannot be exploded by concussion, pressure, friction, shock, or fire.

It does not freeze, and when burned or exploded it does not evolve deleterious fumes. Among other advantages claimed for roburite are that it is practically flameless, so that it can be safely used in fiery mines; that its action is rending, and not pulverizing, which makes it particularly well adapted to quarrying and coal-mining; that it can be detonated at a very low temperature; and finally that it can be exploded only by using a very powerful detonator (one containing at least one gramme of mercury fulminate).

On the other hand, however, on account of the extremely



deliquescent nature of ammonium nitrate, it is necessary to protect the explosive from contact with the air.

In 1887 this explosive was subjected to severe tests by the English Government under the superintendence of Major Sale, R.E., the object of the trials being to compare roburite with guncotton, dynamite, and blasting-gelatine.

Major Sale concluded his report as follows:

"In summing up the results of the foregoing experiments we must bear in mind the great difficulty—we had almost said the impossibility—of obtaining any absolute standard of comparison of the relative strengths of two or more explosives. Each will seem to prove itself superior for certain purposes. Judged, however, by any standard of comparison, it appears that the new explosive has acquitted itself very well, and, especially when we consider its absolute safety, must have a great future before it. Roburite has shown itself to be in some respects more powerful than dynamite, to which it is likely to prove a serious rival in the industrial field, although the latter has the proverbial advantage of strong possession of the ground. An important element in the struggle for ascendancy will be the price at which roburite can be supplied as compared with dynamite, and this will be, we understand, strongly in favor of the new substance.

"But although quite outside the scope of Tuesday's experiments, the great power and safety of roburite seem eminently to fit it for use as a bursting charge for shells, into which its granular form would allow it to be conveniently loaded.

"Much stronger than any picric powder, and doubtless better able to withstand the concussion of the discharge of the gun, an extended series of trials would be necessary to determine the best mode of so employing it."

On account of their peculiar properties bellite, securite, ammonite (or Favier explosives), and roburite are sometimes known as "*safety explosives*."

## LECTURE XI.

### CLASSIFICATION OF THE NITRIC DERIVATIVE CLASS OF EXPLOSIVE COMPOUNDS.

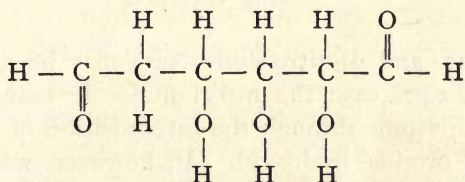
**Nitric Esters. Guncotton.**—The second class of explosive compounds, *nitric derivatives*, may be subdivided into two classes, namely, *nitric ethers* and *nitric esters*, according as they are obtained by the action of nitric acid upon simple or complex alcohols. The equations representing the reactions by which explosives of this class are formed are analogous to those for nitro-substitution compounds, but there are, however, fundamental reactions which characterize the several nitrated products.

As stated in the preceding lecture, there is no reaction nor series of reactions by means of which the original ingredients which combine to form the nitro-substitution product can be reproduced. By treating nitric derivatives, however, with reducing-agents the original ingredients may be reproduced either wholly or in part, according as the derivative is a nitric ether or a nitric ester. In the same lecture the greater stability and energy of nitric derivatives as a class were mentioned and the thermo-chemical reasons therefor were alluded to, as well as other general characteristic properties which might be accounted for by the different arrangement of the atoms in the structure of the explosive molecules. Instead of the nitril molecule or molecules ( $\text{NO}_2$ ) being attached directly to the carbon atoms in the replacement of

such molecules for the hydrogen atoms as in the formation of nitro-substitution compounds, in the nitric-derivatives they are connected through the interposition of an atom of oxygen. We have had occasion to refer to the graphic representation of the explosive molecule, and to suggest the possible effect of the relative position of the replaced atoms upon its stability, as well as other characteristic properties.

For reasons given later on, the constitutional formula for cellulose has not been definitely determined, and although ultimate analysis indicates its composition to be  $C_6H_{10}O_5$ , it is more probable that its true composition is some multiple of this formula, thus,  $nC_6H_{10}O_5$ .

In order to further illustrate the difference in the structure of the nitro-substitution and nitric-derivative molecule, and at the same time suggest a possible explanation of certain anomalies connected with explosives of these classes, we may assume first that the composition of cellulose\* is truly represented by the formula  $C_6H_{10}O_5$ , and if we regard cellulose as an alcohol, as it probably is, the formula may be written  $C_6H_7O_2(OH)_3$ , and graphically represented as follows:



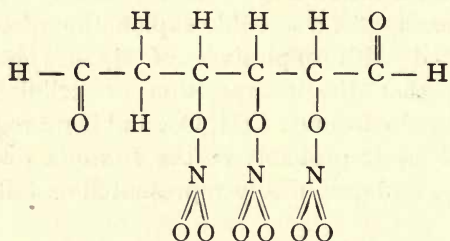
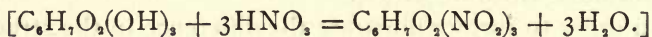
By acting upon cellulose with nitric acid, depending upon the strength of the acid and the period of nitration, one or more atoms of hydrogen are replaced by an equivalent number of molecules of nitryl with the formation of mono-, di-, or tri-nitrocellulose, but so far no higher degree of nitration has been attained than the tri-nitro-derivative. According to the

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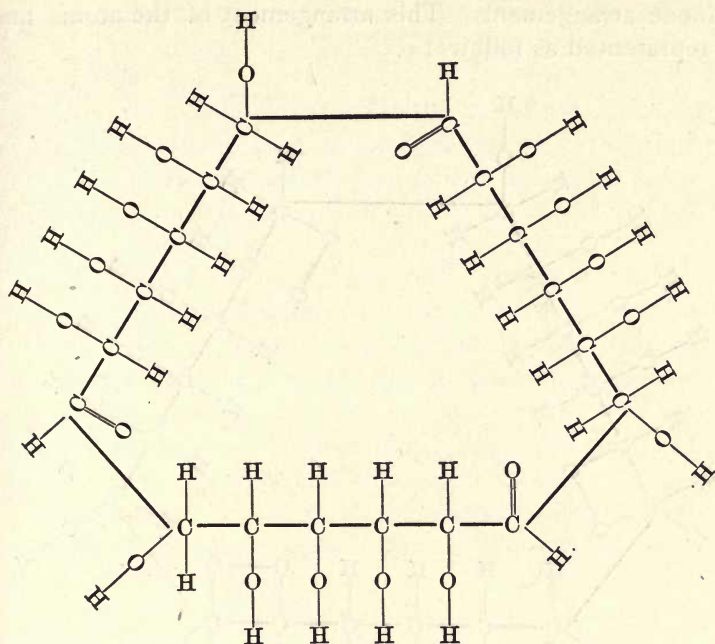
\* This substance is taken for purpose of illustration, because its nitric-derivatives are the most important, as well as the best known, of the class of *nitric-esters*.



constitutional formula for cellulose, there would seem to be no reason why the replacement should be limited to three nitryl molecules for three atoms of hydrogen. If, however, we inspect the graphic formula assumed to represent the molecular structure of cellulose, we observe that three and only three atoms of hydrogen are united so as to form hydroxyl, and if we assume further that it is only the hydroxyl atoms of hydrogen that are replaced by nitryl, and that none others are so replaceable, we have at once a reason for the limit to the possible degree of nitration, and the tri-nitro-derivative should be represented graphically as follows:



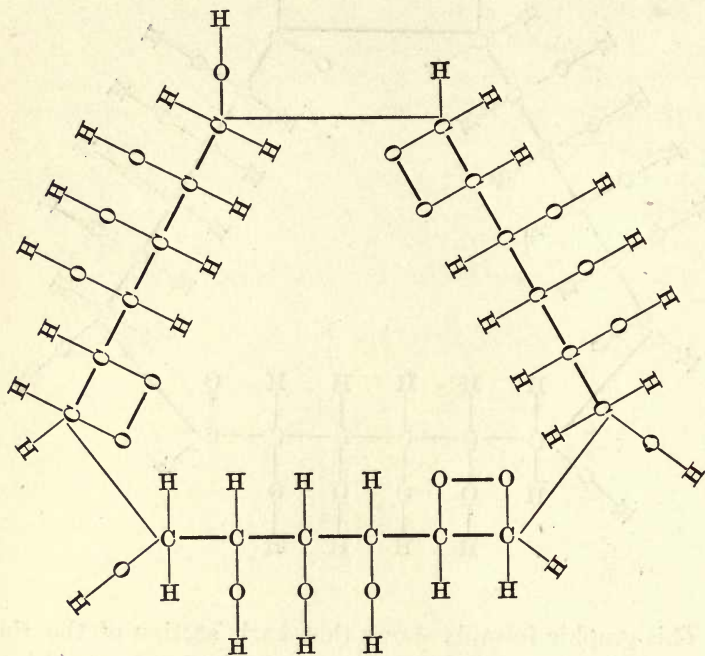
The mono- and di-nitro-derivatives may be similarly represented, in each case the nitryl molecule being connected to the carbon atoms through the interposition of the oxygen-atom of the original hydroxyl. If, however, we assume the composition of cellulose to be represented by a multiple of  $C_6H_{10}O_5$ , as for example by the formulæ,  $C_{12}H_{20}O_{10}$ , or  $C_{18}H_{30}O_{15}$ , the explanation given above is no longer applicable, as is evident from an inspection of the corresponding graphic formulæ. Thus the molecule of  $C_{18}H_{30}O_{15}$  may be represented graphically as follows:



This graphic formula shows that each section of the ring contains four instead of three atoms of hydrogen combined in the form of hydroxyl, and it would seem, following the same line of reasoning, that there should be at least four nitro-derivatives possible; but, as before stated, the highest degree of nitration yet attained is the tri-nitro-compound, the tetra-nitrocellulose as a more highly nitrated product being unknown.

Dr. John W. Mallet offers in explanation of this anomaly the following suggestion, namely, that, instead of four hydrogen atoms being combined in the form of hydroxyl, as represented above, only three hydrogen atoms are so combined, the hydrogen of the fourth hydroxyl molecule being united directly with a carbon atom, while the corresponding oxygen atom and the only other atom of oxygen not combined in the form of hydroxyl are linked together with carbon atoms in the

quinone arrangement. This arrangement of the atoms may be represented as follows:



Accepting the arrangement of the atoms in the molecule as suggested by Dr. Mallet, we again have but three hydroxyl molecules (in each link of the chain), which, together with the hypothesis that only the hydrogen atoms so combined are replaceable by nitryl, explains the limited degree to which this class of substances is susceptible of nitration.

The limitation to the degree of nitration is but one of a number of anomalies presented by the various nitro-substitution products and nitric-derivatives, for which the above suggestions are offered as a possible explanation.

The importance of the positions of the replaced atoms (already mentioned) increases not only with the number of such replacements, but also with the nature of the substituted atoms or radicals. In fact the relative positions may depend



upon the replacing atoms, if dissimilar, since in the substitution they may arrange themselves according to their electrochemical affinities.

Finally, we may have to invoke the aid of *stereo-chemistry*, and apply the principles of stereo-isomerism \* in the arrangement of the atoms in explosive molecules before we arrive at definite and satisfactory explanations of the capricious behavior of the majority of modern high explosives.

**Nitric Esters.**—Logical sequence, as well as the advantage to be gained by dealing with simpler compounds before undertaking more complex combinations, would seem to indicate that nitric ethers should be discussed before entering upon the subject of nitric esters, but priority from an historical point of view and important practical considerations render it more expedient that this order be reversed.

The principal explosives of this class of nitric-derivatives are obtained by acting upon some of the various forms of cellulose with nitric acid.

These compounds, when subjected to the action of water or alkalis, do not undergo simple decomposition with the production of the original cellulose and nitric acid, but give rise to complex reactions, which are very imperfectly known, and have been attributed by some investigators† to the action of an aldehydic compound, cellulose, and its isomeres being alcoholic ethers which are in turn derived from glucose, an aldehydic alcohol.

When treated, however, with reducing agents so as to destroy the nitric acid, nitrocelluloses are decomposed with the reproduction of cellulose, which regains and retains its original properties.

**Guncotton.**—Historically, as well as on account of its great practical value, *guncotton* may be assumed as the type of explosive compounds of the nitric-ester class. As its name implies, guncotton is an explosive made from cotton. It is only necessary to immerse pure dry cotton in a mixture

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\* See results of investigations of Van't Hoff and Le Bel.

† See "Traité élémentaire de Chimie organique," par Berthelot.

of the purest and strongest nitric and sulphuric acids to convert the cotton into guncotton.

The purification of the cotton, the conversion of the cotton into guncotton, and the purification of the guncotton are all somewhat difficult of attainment, and hence the manufacture involves some lengthy and rather complicated processes.

The necessity for these processes and their *rationale* can best be shown by reviewing the history of guncotton, for, in common with most of our modern processes, the present degree of attainment has been reached only through the labors and studies, the failures and successes, of many investigators.

In 1832 Bracconot discovered that when starch, ligneous fibre, and analogous substances were treated with concentrated nitric acid, a highly combustible body, which he termed xyloidine, resulted.

Pelouze repeated these experiments in 1838, and extended his investigations to cotton and paper, which he held were best adapted for the production of this substance. He found that the body could be inflamed at  $180^{\circ}$  C. either by a blow or by a strong pressure, and he recommended its use in pyrotechny. Later, Dumas prepared from paper, by this means, a substance which he called *nitramidine*, and which he proposed for use in making cartridges. The products thus obtained were, however, found to be irregular in composition and unstable, and so no practical result flowed from these researches, until late in 1845, when Schoenbein of Basle announced the discovery of an explosive, which he called guncotton, and which he claimed could be used for all the purposes for which gunpowder was used, while it was four times as powerful as the latter. He kept his method of manufacture secret; but in August, 1846, Boettger of Frankfort proclaimed his ability to make guncotton, and on conferring together it was found that the methods employed were the same, and hence the two formed a partnership for disposing of their secret to the German Government, and the method remained unpublished.

However, on October 5, 1846, Otto of Brunswick gave,

in the *Augsburger Allgemeine Zeitung*, a description of a process for making a guncotton which closely resembled that of Schoenbein's, and which consisted in plunging purified cotton into very concentrated nitric acid for about one-half minute and then washing and drying with great care, while nearly at the same time (1847) W. Knop of Hanover and Taylor of England discovered that guncotton could be prepared by using mixtures of nitric and sulphuric acids.

These discoveries forced Schoenbein and Boettger to reveal their secret, and it was found that they too were using the mixed acids, the proportions being as follows:

	Sp. Gr.	Parts by Weight.	Parts by Volume.
Nitric acid . . . . .	1.45 to 1.50	1	1
Sulphuric acid . . . . .	1.85	3	2.3

The acids were mixed in a porcelain or glass vessel cooled to 10° or 15° C. Then the cotton was plunged in, the proportions being one part of cotton to from twenty to thirty of the acid. After about one hour the cotton was removed, washed in a large quantity of water, then in a solution of potash to remove the last traces of acid, and, finally, with pure water to remove the salts which had been formed. The material was then wrung out, impregnated with a weak solution of saltpetre, again wrung out, and finally dried at a temperature of 65° C.

Taylor's process differed only in using one part of cotton to fourteen of the mixed acids.

Heeren and Karmarsch used one part of fuming nitric acid to two of English sulphuric acid, while Knop used equal volumes of the two acids.

Both of these latter allowed the cotton to remain but from four to five minutes in the acid.

From this time experiments were undertaken in the United States, Germany, France, England, and Russia to test the value of this explosive as a substitute for gunpowder in guns; but the material was found to be unstable, and gave rise to several terrible and at the time inexplicable explo-



sions at Vincennes, Bouchet, and Faversham (1847-1848), which, combined with the grave political disturbances of the time, led to the discontinuance of the experiments, except in Austria, where Baron Von Lenk was engaged in its study.

**Von Lenk's Investigations.**—From a consideration of all the attending circumstances Von Lenk concluded that the accidents above noted were due to the failure to purify the cotton perfectly; or to the use of too weak acids, or too short an immersion, so that the conversion was incomplete; or to the failure to remove the acids completely from the guncotton. The impurities which are present in cotton are of two kinds, natural and artificial. The natural consist of incrusting matter and oily matters; the artificial, of oil and dirt generally, and water.

When impure cotton is immersed in the acid mixture the incrusting substance and greasy matter are acted upon by the acids and form compounds which are quite unstable, and which, if present in the guncotton, may give rise to decomposition in the guncotton itself.

The moisture present serves both to dilute the acid mixture and to cause local heating during immersion, which causes waste of material and may give rise to the formation of unstable compounds which, if present in the guncotton, may also provoke spontaneous decomposition.

The use of weak acids or too short an immersion prevents the complete conversion of the cotton into the stable military guncotton. All chemical reactions require a certain time for their completion, and this is especially the case when the physical structure of either of the reacting bodies is such as to prevent rapid contact between them. The physical structure of cotton is such as to notably prevent the acids from rapidly coming in contact with its parts, for it consists of long, flat, twisted tubes which have been collapsed along their longitudinal axes, so that a cross-section presents the form of a figure eight. It can readily be understood that a considerable time must elapse before the acid can penetrate completely into the interior of such a tube so as to convert

all its substance into guncotton. For the same reason it will be understood that it must be very difficult to expel the last traces of acid from the capillary tubes, yet if any trace of acid remains in them it is likely to provoke progressive decomposition in the guncotton.

**Von Lenk's Process.**—This consisted in—

1st. *The cleansing and perfect desiccation of the cotton.* The cleansing was effected by first removing the dirt and knots by mechanical means, then immersing the cotton in small portions for two or three minutes in a boiling solution of caustic potash (sp. gr. 1.021) in order to remove the fatty matters and incrusting substances, then removing the potash liquor by means of a centrifugal machine, and washing with pure water and finally drying at 95° F. At ordinary temperatures cotton-wool exposed to the air absorbs 6 per cent of moisture.

2d. *The employment of the strongest acids attainable in commerce.* These consisted of nitric acid sp. gr. 1.48 to 1.49 at 17°.5 C. and sulphuric acid sp. gr. 1.835, mixed in the proportions of one part by weight of nitric to three parts by weight of sulphuric.

3d. *The steeping of the cotton in a fresh strong mixture of acids, after its first immersion and partial conversion into guncotton.* A pot holding about 60 pounds of the acid mixture was used for the dipping, and two skeins (about 3 ounces) of cotton were dipped at each operation. After some minutes the partially converted cotton was removed from the pot, placed upon a rack, and squeezed until one part of the cotton contained about ten and one half parts of acid. The pressed cotton was now placed in a steeping-pot and fresh acid poured over it, while the dipping-pot was filled to its original level with acid.

4th. *The continuance of the steeping for twenty-four to forty-eight hours.* After the guncotton had been placed in the steeping-pot and the acid added, the guncotton was pressed to the bottom of the pot, so that it would be completely covered with the acid, the pot was then covered, placed in a

trough of cool water and allowed to remain for the time stated.

5th. *The thorough purification of the guncotton so produced from every trace of free acid.* To effect this the guncotton was placed in a centrifugal machine, revolving at about 800 turns per minute, and in about ten minutes the acid present was reduced so that about one pound of the guncotton contained but three pounds of acid.

The guncotton was then plunged into a cascade of water and washed in a running stream of water for from three to six weeks, and then treated with a weak solution of boiling potash, washed and dried in free air at 25° C. Then the guncotton was immersed for some time in a solution of sodium silicate (sp. gr. 1.072), wrung, and exposed for three days to free air, again washed, wrung and dried, first in free air, and finally in a chamber whose temperature did not exceed 35° C.

Von Lenk began the manufacture at Heitenberg, near Wiener-Neustadt, about 1853, and continued to direct the factory up to 1865, during which time considerable quantities of the material were made. Extensive experiments, on its value as a substitute for gunpowder as a projecting agent, were conducted with it, and the results were so favorable that the Austrians supplied thirty batteries with guncotton cartridges, and the explosive bid fair to soon be adopted as a service explosive; but, unfortunately, two serious explosions during storage occurred, one at the magazine at Simmering in 1862, the other at the magazine of Steinfeld in 1865, and these combined with the fact that the explosive, in spite of the precautions taken, often developed abnormal pressures in the guns led to its use being interdicted.

**Abel's Improvements and Patents.**—Von Lenk patented his process in England in 1862, and in 1864 the Prentice Brothers began the manufacture of guncotton under this process at Stowmarket.

In 1865 Abel patented his improvement on the process. This consisted in reducing the guncotton to a pulp, and then



by moulding and pressure converting it into such forms and masses as were desired for use. The pulping was effected by a rag-engine or pulper, such as is used in converting the rags used in making paper into pulp.

The advantage gained by this is, *first*, that the guncotton tubes are cut into such short lengths that the acid and foreign matters can be easily and completely removed from the fibre; *second*, that cotton waste, a cheaper material, can be used for the manufacture; and *third*, since the pulped material can be pressed, it is possible to impart to the final product a high density and thus obtain a large weight of the explosive in a small volume.

Abel's modifications were shortly afterwards adopted at Stowmarket, and the manufacture and use were successfully pursued without accident until August, 1871, when 13½ tons of the compressed guncotton which were stowed in the packing-house at Stowmarket exploded. A very thorough investigation of the circumstances attending this explosion was made, and as a result the jury found "that the accident was due to the spontaneous explosion of some impure guncotton, the impurity consisting in the presence of a large quantity of sulphuric acid, or of mixed sulphuric and nitric acids, which acids were wilfully added by some person or persons unknown, after the guncotton had passed through the regular process of manufacture and testing." Since then we have no record of any spontaneous explosions having occurred, and it is very unlikely that they should have taken place, for, thanks to Brown's discovery, the finished product is now almost wholly stored in the wet state. Shortly after the Stowmarket explosion the English Government erected works at Waltham Abbey, and the French at Moulin-Blanc, and the other European governments followed suit, all of them adopting Von Lenk's process with Abel's modifications.

**Adoption of Guncotton in this Country as a Service Explosive.**—As has been said above, experiments were made in this country, not long after the discovery of guncotton, to test its value as a projecting charge in guns, but they were

soon abandoned, as the material was found to be too unsafe for use in this way.

Experiments were, however, begun at the U. S. Torpedo Station by Professor Hill in 1872 to test the value of the compressed guncotton, as made by Abel's process, for the use of the torpedo service, and the experiments were continued up to 1883, and on November 14 of that year a guncotton torpedo outfit was issued to the U. S. S. Trenton and the material was adopted as a service explosive in the United States Navy.

The guncotton used in these experiments was obtained from Stowmarket, and that issued to the Trenton was in the form of cylindrical disks three inches in diameter and two inches high.

Guncotton having been adopted as a service explosive, it was not deemed prudent to depend upon foreign sources for our supply; a plant for the manufacture of the explosive was therefore installed at the U. S. Naval Torpedo Station, and the manufacture of gun-cotton was begun early in 1884, and continued in successful operation until the factory was destroyed by fire in 1893. This factory has been restored, and, together with the DuPont plant, continues to supply the highest grade of guncotton in such quantities as to meet all demands.\*

**Chemistry of Guncotton.**—From its reactions cellulose may be regarded as an alcohol, but owing to the fact that cellulose is a non-volatile solid, its vapor density, and therefore its molecular weight, has never been determined, and consequently its molecular constitution is unknown. Its ultimate analysis, however, leads to the simplest empirical formula of  $C_6H_{10}O_5$ , but it is probable that its true molecular constitution should be represented by some multiple of this expression.

When cellulose is acted upon by nitric acid or mixtures of nitric and sulphuric acids, the hydrogen of the hydroxyl is replaced, more or less completely, by  $NO_2$ , and in this way various cellulose nitrates may be obtained. The composition

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\* The American Smokeless Powder Co. is now producing an excellent grade of guncotton which is fully up to the highest standard.

of the products resulting from this action depends upon the strength of the acids employed, the proportions of acid used, the temperature during immersion, and the time of immersion. If the acids are as follows:

	Sp. Gr.	Parts by Weight.
HNO <sub>3</sub> .....	1.50	1
H <sub>2</sub> SO <sub>4</sub> .....	1.85	3

—the proportions of cellulose to acid is as 1 : 300, the time of immersion ten minutes, the time of steeping forty-eight hours, and the temperature about 15° C.; then we ought to obtain the most complete conversion of the cellulose, and, if we assume the lowest multiple of the above expression to represent the composition of cellulose, the reaction would be expressed by the following equation,  $C_6H_7O_2(OH)_3 + 3HO.NO_2 = (C_6H_7O_2)_3O_3(NO_2)_3 + 3H_2O$ . The cellulose thus obtained is familiarly known as "*tri-nitrocellulose*," and, according to Abel, it is the principal constituent of the military guncotton. Theoretically, 100 parts of cellulose should yield when properly nitrated 183.5 parts of tri-nitrocellulose; practically, the yield is about 155 parts of explosive from every 100 parts of thoroughly dried cotton.

In his investigation Eder discovered a form of nitrocellulose in which the percentage of nitrogen lay between that contained in the di-nitro- and tri-nitro-compounds. He therefore assumed the formula for cellulose to be  $C_{12}H_{20}O_6$ , but failed to obtain or recognize the mono-nitro-derivative.

Vieille carried his investigations even further, and obtained various forms of nitrocellulose under extremely different conditions, and, as a result of his experiments, assumed a still higher multiple of  $C_6H_{10}O_5$ , namely,  $C_{24}H_{40}O_{20}$ , as the constitutional formula for cellulose. Although the mono-nitro-derivative has never been obtained alone, it appears to be formed in connection with the higher nitro-compounds during the process of nitration. The various forms of nitro-cellulose together with the percentage of nitrogen in each, may therefore be enumerated as follows:



From  $C_6H_{10}O_5$ ,

$(C_6H_7O_2)O_3(NO_2)H_2$	=	mono-nitrocellulose with	7.34	per cent of N
$(C_6H_7O_2)O_3(NO_2)_2H$	=	di-nitrocellulose	11.13	" " " "
$(C_6H_7O_2)O_3(NO_2)_3$	=	tri-nitrocellulose	14.14	" " " "

From  $C_{12}H_{20}O_{10}$ ,

$(C_{12}H_{14}O_4)O_6(NO_2)_2H_4$	=	di-nitrocellulose with	6.76	per cent of N
$(C_{12}H_{14}O_4)O_6(NO_2)_3H_3$	=	tri-nitrocellulose	9.15	" " " "
$(C_{12}H_{14}O_4)O_6(NO_2)_4H_2$	=	tetra-nitrocellulose	11.11	" " " "
$(C_{12}H_{14}O_4)O_6(NO_2)_5H$	=	penta-nitrocellulose	12.75	" " " "
$(C_{12}H_{14}O_4)O_6(NO_2)_6$	=	hexa-nitrocellulose	14.14	" " " "

From  $C_{24}H_{40}O_{20}$ ,

$(C_{24}H_{28}O_8)O_{12}(NO_2)_4H_8$	=	tetra-nitrocellulose with	6.76	per cent of N
$(C_{24}H_{28}O_8)O_{12}(NO_2)_5H_7$	=	penta-nitrocellulose	8.02	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_6H_6$	=	hexa-nitrocellulose	9.15	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_7H_5$	=	hepta-nitrocellulose	10.18	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_8H_4$	=	octo-nitrocellulose	11.11	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_9H_3$	=	mono-nitrocellulose	11.96	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_{10}H_2$	=	deca-nitrocellulose	12.75	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_{11}H$	=	endeca-nitrocellulose	13.47	" " " "
$(C_{24}H_{28}O_8)O_{12}(NO_2)_{12}$	=	dodeca-nitrocellulose	14.14	" " " "

The highest grades of nitrocellulose are obtained only by using the purest and most concentrated acids, and by subjecting the cellulose, which must be thoroughly cleaned and dried beforehand, to the action of the acids for a considerable length of time. The highest degree of nitration of which cellulose is susceptible, or, in other words, the highest grade of cellulose nitrate obtainable, depends upon the formula assumed to represent the original cellulose. There appears to be no doubt that a nitrate of cellulose may be produced containing a higher percentage of nitrogen than can possibly exist in the most highly nitrated product obtainable from cellulose represented by Vieille's formula. The weight of evidence points to  $C_{18}H_{21}O_6(OH)_3$  or some higher multiple than  $4(C_6H_{10}O_5)$  as the most probable constitution of cellulose. The lower grades of nitrocellulose are prepared by using weaker acids or other modifications in the process of nitration.

The tri-nitrocellulose of Abel, which corresponds exactly with Eder's hexa-nitrate and the deca- and endeca-nitrates of Vieille, are known as military guncotton, and are characterized

by their insolubility in the ether-alcohol mixture (one volume of absolute alcohol, sp. gr. 0.805, to two volumes of strongest ether, sp. gr. 0.735); the endeca-nitrocellulose is, however, completely dissolved by ethyl acetate. Of the other cellulose nitrates, the di-, octo-, and mono-nitro-compounds are readily soluble in the ether-alcohol mixture as well as in ethyl acetate (acetic ether); the hepta-nitrate, when treated with these solvents, gelatinizes, but does not dissolve entirely; of the other derivatives of Vieille, subjected to the action of the same agents, the hexa-nitrate swells up without dissolving in ethyl acetate, and is unaffected by the mixture, while the penta- and tetra-nitrates are scarcely affected. As has been said, the tri-nitrocellulose of Abel, the hexa-nitrocellulose of Eder, and the deca- and endeca-nitrocelluloses of Vieille are known as guncotton, while the other cellulose nitrates are known as pyroxyline and collodion guncotton.

Collodion guncotton is so called from the fact that the solution which it forms with ether-alcohol, when exposed to the air, gives up its ether and alcohol by volatilization and deposits its guncotton as a gummy, collodial, strongly adhesive film on the body with which it is contact. This solution, known as collodion, is employed for coating the surfaces of the plates used in the wet process of photography, and it is also used in surgery to produce an artificial skin over cuts and wounds.

**Properties of Guncotton.**—The fibrous guncotton seen in ordinary light differs little, if any, in appearance, even when examined under a microscope, from the cotton from which it is made, but, if seen under the microscope by polarized light, the fibres of guncotton appear dull and only feebly colored, while cotton fibres, under the same circumstances, are brilliant in lustre and iridescent.

Guncotton is harsher to the touch and less flexible than cotton; when dry it becomes quite highly electrified if rubbed between the fingers, and is luminous when rubbed in the dark.

Guncotton is completely insoluble in water, either hot or cold.

The action of ethyl acetate and of ether-alcohol upon it and the pyroxylin has been noted above.

Guncotton is also soluble in a mixture of ether and ammonia and in acetone  $[(CH_3)_2CO]$ . All the cellulose nitrates are soluble in a strong solution of sodium hydroxide, undergoing a partial saponification, with the formation of cellulose and sodium nitrate. Concentrated sulphuric acid displaces the nitric acid even in the cold. Reducing agents, such as ferrous chloride or acetate, or the alkaline sulphyroxides, especially in alcoholic solution, convert the cellulose nitrates into cellulose, even by digestion at ordinary temperatures. By boiling with a solution of stannous oxide in potassium hydroxide the cellulose nitrates are dissolved and the cellulose is reduced and may be precipitated in flocks on neutralizing the liquid. These reactions are often employed in the analysis of the cellulose nitrates. The density of guncotton varies with the mode of preparation and the amount of compression to which it is subjected. It averages about 0.1 to 0.3 for guncotton in the form of flocks or fibre, and is about 1.1 for the dry compressed Abel guncotton. Experiments made at L'École de Pyrotechnie de Toulon (1870) showed that the pressure to be applied increases much more rapidly than the density of the resulting product, and that it is impracticable to carry the density above 1.4 to 1.5.

Guncotton is said to be less hygroscopic than either ordinary cotton or than gunpowder. The normal humidity of air-dry guncotton is put at 1.5 to 2 per cent, though it is believed that by prolonged exposure to a saturated atmosphere it may reach 2.75 per cent, but this does not appear to have any marked effect on its inflammability. According to Beckerhinn an increase in the percentage of moisture in guncotton used for projecting charges causes a more rapid fall in the pressure produced than in the initial velocities given, which, if true, gives a means for neutralizing the brisant effect of guncotton on the piece, while leaving us a ballistic medium much superior in power to ordinary gunpowder.

It is claimed that guncotton is not susceptible, even when



dry, to pressure, percussion, or friction, unless it be strongly confined and firmly compressed, and the heat developed is very considerable, but experiments in this laboratory tend to disprove this claim.

To explode dry guncotton by percussion with some degree of certainty, it is necessary to take a very small piece, wrap it tightly in tin-foil, place it on an anvil, strike it several light blows to compress it, and then a heavy blow. If the latter is not fair it will fail to effect the result. As will be seen later, shell filled with disks of dry guncotton have been fired from 24-pounders with service charges of powder into the masonry escarpment of the fort on Rose Island at a distance of 50 yards from the muzzle of the gun, where the shell were completely broken up on impact without any of the guncotton having been exploded.

The wet guncotton is in the process of pressing subjected to a pressure of about 6300 pounds per square inch; and the pressure has been carried to over 13,000 pounds without causing explosion.

If a flame or any incandescent body is applied to dry loose guncotton, the latter burns with a flash but without explosion. If the guncotton is woven or twisted tightly, the speed of combustion is very much reduced, and when the guncotton is pulped and compressed, the rate of combustion is reduced still more. If water is poured on a disk or block of burning guncotton, the flame may be extinguished, though sometimes, when the fire is inside, it can be reached only with difficulty.

If the mass of burning guncotton is very large, it is possible that an explosion may take place from the outer parts furnishing sufficient confinement to the inner.

Wet compressed guncotton cannot be set on fire until the moisture is dried out of it. If a wet disk or block be placed in a fire, the outer surface will dry and be slowly consumed, and this will continue, layer by layer, until the whole is consumed. As much as 2000 pounds of wet guncotton has been placed in a bonfire, where it slowly burned away without explosion. The point of explosion of guncotton and py-

roxylin naturally vary somewhat, but that of guncotton may be taken as about  $182^{\circ}$  C. ( $360^{\circ}$  F.).

Considerable apprehension exists in the minds of many who are not intimately acquainted with the substance, regarding guncotton, and they are apt to fear that, through decomposition during storage or transportation, or by the action of ordinary shocks, heat, or pressure, it may accidentally explode.

These apprehensions have arisen from the many accidents which have occurred in the history of the explosive, some of which have been noticed already, and which, as has been pointed out, were due to the impurities existing in the guncotton as a necessary result of the imperfect processes of manufacture followed, and these apprehensions are strengthened by the many accidents which have occurred in the past, and still do occur, with other high explosives, and which many appear to think are a necessary consequence of their use.

While guncotton is a powerful explosive, and in fact a high explosive, and necessarily dangerous, as all explosives must be; yet when handled, used, and stored as directed, it is the safest explosive known, and when properly made is absolutely free from any tendency to undergo dangerous decomposition.

**Decomposition of Guncotton.**—When guncotton is decomposing it first begins to give off nitrous fumes, and eventually yields them in such quantity as to color the surrounding atmosphere a deep brownish red. At the same time the guncotton begins to show pasty yellow spots, and eventually the whole becomes converted into a pasty yellow mass, which first shrinks to about one tenth of the volume of the original guncotton, and then swells up as the gas is evolved. Next the mass shrinks again, and becomes converted into a gummy residue having a very much smaller volume than the guncotton from which it was formed, and finally it dries up to a brown horn-like mass.

This decomposition results in the formation from the guncotton of oxides of nitrogen, formic and acetic acids, which

are evolved as vapors, and an amorphous, porous, sugar-like body almost entirely soluble in water, which contains a considerable quantity of glucose, gummy matter, and oxalic acid, and a small quantity of formic acid, and of pectic and para- and meta-pectic acids. Changes such as these just described have repeatedly taken place under my own observation with guncotton which has been imperfectly freed from acid, or with pyroxylin, and many other chemists have observed them, and in none of these cases did an explosion, or anything approaching an explosion, take place.

The decomposing effects of acids may also be witnessed at the U. S. Naval Torpedo Station on any Saturday while the guncotton factory is in operation, for it is the custom at that time to take the waste sweepings of the factory, which have accumulated during the week, to the beach, and to pour upon them a quantity of the waste acid mixture.

Soon after the acid is poured on the mass begins to yield copious quantities of oxides of nitrogen (or, as the workmen technically say, "firing" takes place) and the mass undergoes the changes described above, but no explosion ensues. These observations have been made on guncotton decomposing when unconfined or when loosely confined. It is of course obvious that if the guncotton was confined in a tight receptacle the gases evolved during decomposition might generate pressure enough to burst the receptacle and thus produce an explosion.

Again, as heat is produced by the chemical reaction, it might be possible that when the guncotton is confined the heat generated cannot be conveyed away as fast as generated, and that in consequence the temperature continually increases so that it eventually reaches the ignition-point of the explosive; then, of course, an explosion might ensue: and this is the probable explanation of the origin of the explosions noted as occurring in the magazines at Stowmarket and elsewhere. The decompositions described have, with the exception of the destruction of the waste at this station, been observed to take place only in dry guncotton or pyroxylin.



To produce it in wet guncotton it is necessary that the amount of acid present should be very much in excess of the guncotton with which it is in contact; hence the development of such slight traces of acid during the storage of wet compressed guncotton as have been observed by Abel is not likely to produce dangerous decomposition, while, besides, the water present tends to prevent any considerable rise in temperature.

It is well known that light rays sometimes play an important part in inducing chemical changes. We have only to cite the well-known cases of the decomposition of carbon dioxide within the leaf-cells of plants, or of the silver salts in the photographic plate, or better, in this connection, the decomposition of the amides. It is not to be wondered at that it should be believed and expected that guncotton would also be susceptible to the action of light, especially since Tyndall has shown that nitrous esters like the amyl and butyl nitrites may be decomposed by the action of a beam of light. The literature of guncotton and pyroxylin is full of the most conflicting statements regarding the effect of light upon them, but this is not surprising when we consider the great variety of substances employed and their varying degrees of purity as made by different methods. Guncotton produced from properly purified cotton, according to the directions given by Von Lenk, may be exposed to diffused daylight, either in open air or in closed vessels, for very long periods without undergoing any change.

The preservation of the material for three and one-half years under these conditions has been perfect. Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in guncotton of the description defined above; and the statements which have been published regarding the very rapid decomposition of guncotton when exposed to sunlight do not therefore apply to the nearly pure cellulose nitrate obtained by strictly following the system of manufacture now adopted. If guncotton in closed vessels is left for protracted

periods exposed to strong daylight and sunlight in a moist or damp condition it is affected to a somewhat greater extent; but even under these circumstances the change produced in the guncotton by several months' exposure is of a very trifling nature.

Singularly enough it has been found that guncotton which had been freely exposed to air and diffused sunlight for about twelve months had its stability, as determined by the heat test, very materially raised. Guncotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed in boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary storehouses (as far as an experience of three and one-half years has shown). Guncotton prepared and purified according to the prescribed system and stored in the ordinary dry condition does not furnish any indication of alteration beyond the development, shortly after it is first packed, of a slight peculiar odor, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

Abel has studied the effects of heat upon both dry and wet guncotton, and he finds that the influence exerted upon the stability of guncotton of average quality, as obtained by strict adherence to Von Lenk's system of manufacture, by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates is very trifling, and it may be so perfectly counteracted by very simple means, which in no way interfere with the essential qualities of the material, that the storage and transportation of guncotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident, than is the case with gunpowder. Perfectly pure guncotton resists to a remarkable extent the destructive effects of temperatures, even those approaching  $100^{\circ}\text{C.}$ , and the lower cellulose nitrates (soluble guncotton or pyroxylin) are at any rate not more prone to alteration when pure. The incomplete conversion of cotton into the most explosive product does not, therefore, of necessity result in

the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid mixture.

But all ordinary products of manufacture contain small proportions of organic nitrogenized impurities of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matters retained by the cotton fibre, and which are not completely separated by the ordinary or even a more searching process of purification.

It is the presence of this class of impurities in guncotton which first give rise to the development of free acid when the substance is exposed to the action of heat; and it is the acid thus generated which eventually exerts a destructive action upon the cellulose products, and thus establishes decomposition which is materially accelerated by heat. If the small quantity of acid developed by the impurity in question be neutralized as it becomes nascent no injurious action upon the guncotton results, and the great promoting cause of the decomposition of guncotton by heat is removed.

This result is readily attained by uniformly distributing through guncotton a small proportion of a carbonate, the sodium carbonate applied in the form of a solution being best adapted to this purpose. The introduction into finished guncotton of one per cent of sodium carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated temperatures as would induce some decomposition in the perfectly pure cellulose products. That proportion affords, therefore, security to guncotton against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to guncotton might exert upon its properties as an explosive would consist of a trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

It has been observed that when dry guncotton is freely



exposed to air in an atmosphere of a temperature of about  $45^{\circ}$  C. for about three months, its stability, as determined by the heat test, is materially raised—just as Abel found it to be for exposure to diffused daylight.

Water acts as a most perfect protection to guncotton (except when it is exposed to sunlight) even under extremely severe conditions of exposure to heat. An atmosphere saturated with aqueous vapor suffices to protect it from change at elevated temperatures, and wet or damp guncotton may be exposed for long periods in confined spaces at  $100^{\circ}$  C. without sustaining any change. Actual immersion in water is not necessary for the most perfect preservation of guncotton; the material, if only damp to the touch, sustains not the slightest change even if closely packed in large quantities. The organic impurities which doubtless give rise to the very slight development of acid when guncotton is closely packed in the dry condition appear equally protected by the water, for damp and wet guncotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from the guncotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient, not only to act as a perfect protective, but also to guard against all risk of accident.

It is therefore in this wet condition that all reserve stores of the substance should be preserved, or that it should be transported in large quantities. If the proper proportion of sodium carbonate be dissolved in the water with which the guncotton is originally saturated for the purpose of obtaining it in this non-explosive form, the material, whenever it is dried for conversion into cartridges, or employment in other ways, will contain the alkaline matter required for its safe storage and use in the dry condition in all climates. Cold has no effect upon dry guncotton, but of course if low enough it may freeze the water in the wet guncotton, and when the latter is in the form of compressed pulp, as now

issued, the freezing will cause flaking, cracking, and breaking down of the physical structure, with a consequent reduction in density; hence freezing is to be avoided if possible. Alternate changes from heat to cold and the reverse, unless excessive, have little effect on the physical structure and none on the chemical stability of guncotton.

**Explosive Effect of Guncotton.**—From what has been said with respect to the products of explosion of gunpowder, it might be expected that those furnished by guncotton would vary according to the conditions under which the explosion takes place. When a mass of the guncotton wool is exploded in an unconfined state the explosion is comparatively slow (though appearing to the eye almost instantaneous), since each particle is fired by the flame of that immediately adjoining it, the heated gas (or flame) escaping outwards, so that some time elapses before the interior of the mass is ignited. But when the guncotton is inclosed in a strong case, so that the flame from the portion first ignited is unable to escape outwards and must spread into the interior of the mass, this is ignited simultaneously at a great number of points, and the decomposition takes place far more rapidly; a given weight of guncotton being thus consumed in a much shorter time, a far higher temperature is produced, and the ultimate results of the explosion are much less complex, as would be expected from the well-known simplifying effect of high temperatures on chemical compounds.

Although the products of combustion of guncotton have been made the object of special study and investigation, the results have varied between wide limits, due to the fact that the exact composition of the explosive used in the experiments has almost invariably been more or less a matter of conjecture. The volume of permanent gases evolved by the explosion of one gramme of guncotton has thus varied from 483 c.c. (Teschenmacher and Porret) to 829 c.c. (Károlyi), both volumes being reduced to 0° C. and 760 mm.

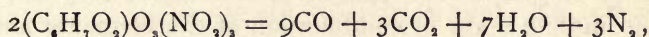
The composition of the permanent gases, when the de-

composition of the explosive occurred *in vacuo*, was found to be as follows:

	Hecker and Schmidt.	Teschenmacher and Porret.	Karolyi.	Berthelot.
Carbonic oxide.....	37.91%	19.02%	28.55%	41.9%
“ acid.....	13.32	7.63	19.11	18.40
Marsh-gas.....	....	....	11.17	1.30
Olefiant gas.....	4.36	....	....	....
Cyanide.....	....	3.79	....	....
Nitric oxide.....	15.35	18.08	8.83	24.70
Nitrogen.....	4.03	3.82	8.56	5.80
Aqueous vapor.....	24.76	47.66	21.93	....
Hydrogen.....	....	....	....	7.90
	100.00	100.00	98.15	100.00

The determination of the products of explosion of confined guncotton was effected by Karolyi by inclosing the guncotton in a cast-iron cylinder strong enough to resist bursting, until the combustion of the last portion of the charge (which was suspended in an iron globe exhausted of air, and exploded by a galvanic battery) was complete; the total volume of the resulting gases was then measured and subjected to analysis.

Unfortunately, the cellulose nitrate used by Karolyi was not pure guncotton, so his results are but roughly approximate; still they indicate that the reaction might proceed according to the following equation:



although, naturally, no single equation would be likely to represent the complex reactions involved in an explosion by ignition. From this equation we deduce that one gramme of guncotton yields 829 c.c. of gas at  $0^\circ$  and 76 cm., or, with one cubic centimetre of compressed guncotton having a density of unity, one volume of this guncotton would yield 829 volumes of gas.

From his experiments Karolyi found that the state of



the gases depends upon the pressure and temperature of the explosion. He accounted for the absence of nitric oxide when the explosion or decomposition occurred under high pressure upon the assumption that at increased temperatures hydrogen and marsh-gas acted as reducing agents, and, taking oxygen from the nitric oxide, contributed to the formation of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ , with the liberation of free  $\text{N}$ .

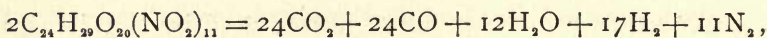
As the result of their investigations, Sarrau and Vieille have determined the total heat of combustion to be for 1143 grammes of explosive 633 cal.

The heat of formation from its elements would be 624 cal. for the same quantity of explosive (Berthelot).

Roux and Sarrau have determined the temperature of the gaseous products of guncotton at the moment of explosion to be  $3700^\circ \text{C}$ ., while the experiments of Nobel and Abel indicate the maximum temperature to be  $4400^\circ \text{C}$ .

In their investigations Sarrau and Vieille found that at high pressure the aqueous vapor was dissociated and more carbonic acid formed.

Accepting Vieille's formula for the composition of guncotton, this may be represented by the equation



and by calculation we find that the initial pressure exerted by guncotton is over three times that of gunpowder, and that, like that of gunpowder, the effect is reduced in practice by the incomplete state of combination of the elements and the complexity of the products which they tend to form, and the result is that the impact becomes less brusque and more regular as the combination becomes more complete during cooling.

From the data already given the explosive force of guncotton may be readily calculated. Berthelot estimates the pressure developed by the detonation of guncotton, of density 1.1 under constant volume, to be 24,000 atmospheres, or about 160 tons per square inch.

Sebert finds the rate of propagation of the detonation, when the guncotton is confined in tubes of tin, to be from 5000 to 6000 metres per second, while it is but 4000 in tubes of lead. Piobert found the rate of inflammation in flocculent guncotton in free air to be eight times that of gunpowder.

The value of guncotton as a military explosive was much enhanced by the discovery, made in 1868 by E. O. Brown, of the Chemical Department at Woolwich, that it could be detonated, even when unconfined, by means of a small charge of mercury fulminate, and that it could even be so detonated when thoroughly saturated with water if only a small initial charge of dry guncotton be detonated in contact with it; and this is the method which is now universally used for producing the explosion of compressed guncotton, for not only is it easy of application and enables us to explode guncotton when wet, but causes the explosive to develop the maximum force in a very small interval of time, and thus to produce that crushing effect which is desirable in a torpedo explosive.

The results of experiment show that thoroughly dry guncotton may be detonated by three grains of mercury fulminate, and air-dried guncotton by five grains, provided the fulminate is well confined in copper cases, and the cases are in intimate contact with the guncotton.

These conditions are important to success. Notwithstanding so small a quantity can effect the detonation, thirty-five grains of the fulminate are used in the U. S. Navy detonators which are used with the naval torpedo system.

When guncotton or any other high explosive is tamped, we obtain a more violent disruptive effect through its detonation than when it is untamped, for confinement brings about the most complete decomposition. When freely exposed to the air, guncotton is supposed to be untamped; but this is not strictly true with this or any other high explosive, for it acts so quickly as to violently disturb and set in motion a very considerable mass of the atmosphere, and this atmosphere acts as a tamp.

Wet guncotton appears to be a more violent disruptive

agent when detonated than dry guncotton, and this notwithstanding that its combustion is not so complete. This fact has been explained by supposing that the water in its pores, being nearly incompressible and highly elastic, increases the rate of propagation of the explosive reaction, and hence diminishes the time factor.

*Soluble Guncotton, or Collodion-cotton.*—In the manufacture of military guncotton various other forms of nitrocellulose are formed, which on account of their ready solubility in the ether-alcohol mixture, as well as in other solvents, are known under the generic term of soluble guncotton, or collodion-cotton. In addition to existing as by-products in the manufacture of the military explosive, soluble guncotton, on account of its importance in several industries, is manufactured very extensively on a commercial scale. The principle involved in the process of manufacture is identical with that already stated in the case of the more highly nitrated product.

According to Eder's formulæ, there are four varieties of soluble guncotton, viz., di-nitro-, tri-nitro-, tetra-nitro-, and penta-nitrocellulose, any one of which may be obtained by varying the strength of the acids, the temperature of the acid mixture, or the period of nitration.

The acid mixture most generally adopted is as follows:

$\text{HNO}_3$ (sp. gr. 1.44).....	1 part
$\text{H}_2\text{SO}_4$ (sp. gr. 1.84).....	1 “

During the process of nitration, which lasts from one-half to one and one-half hours, the temperature of the acid mixture is kept at about  $40^\circ \text{C}$ . In every other respect the process of conversion, extraction, washing, etc., is identical with that to be described in the following lecture.

**Nitro-hydrocellulose.**—By treating cellulose with dilute sulphuric or hydrochloric acid, it absorbs water and is reduced to a very fine powder, in which form it is very readily nitrated. The resulting powder is called hydrocellulose (Aimé Girard), and the nitrated product obtained by treating it with nitric acid is known as nitro-hydrocellulose. The usual method of



manufacture is to steep the carefully prepared cotton for a few minutes in an acid mixture consisting of

$\text{H}_2\text{SO}_4$ (sp. gr. 1.84) .....	3 parts
$\text{H}_2\text{O}$ .....	97 “

or

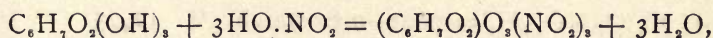
$\text{HCl}$ (sp. gr. 1.20) .....	3 “
$\text{H}_2\text{O}$ .....	97 “

It is then freed from acid and dried, and as soon as dry it readily breaks up and forms a pulverulent mass. By using stronger acids and immersing the cotton for twelve hours, the conversion into hydrocellulose proceeds quietly, and forms into a compact body at the bottom of the trough or jar, from which the supernatant acid mixture may be separated by decantation, and the mass washed and rewashed in the same vessel until entirely free from acid. When dry the cake is easily reduced to powder by sieving or other means.

The subsequent process of nitrating the hydrocellulose is similar in every respect to that to be described in the case of guncotton, with the exception that no pulping is necessary, and the resulting guncotton is very uniform and of a very high grade.

Nitro-hydrocellulose is more sensitive to shock than ordinary guncotton, and its use has as yet been limited to the manufacture of detonating fuses and primers for blasting gelatine

**Nitro-starch.**—The composition of starch is identical with that of cellulose,  $n\text{C}_6\text{H}_{10}\text{O}_5$ , and by subjecting it to the action of nitric acid analogous nitric derivatives are obtained. Thus, assuming  $n$  to be unity, since its exact value is not yet definitely known, the equation representing the reaction may be written as follows:



which is identical with that representing the conversion of cotton into guncotton. By varying the strength of the nitric

acid, and modifying other conditions, the lower grades, mono-nitro- and di-nitrostarch, may be obtained. For mechanical reasons it is found advisable not to introduce the starch into a mixture of nitric and sulphuric acids as in the case of nitrating cotton, but to dissolve the starch in nitric acid first, and then introduce the solution, when cool, into the mixed acids.

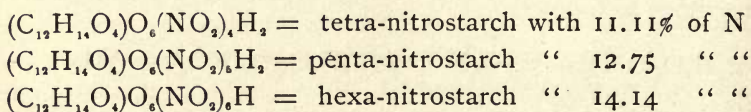
Practically the following proportions have been found to give good results:

Solution	{ Starch .....	1 part
	{ $\text{HNO}_3$ (sp. gr. 1.50) .....	10 parts
Acid mixture	{ $\text{HNO}_3$ (sp. gr. 1.06) .....	1 part
	{ $\text{H}_2\text{SO}_4$ (sp. gr. 1.62) .....	2 parts
Solution .....		1 part
Acid mixture .....		5 parts

Waste acids from the manufacture of nitroglycerine, to which about 20% of water is added, may be used for the acid mixture.

The starch solution is introduced into the mixed acids in a finely divided state, and the nitrostarch forms as a pulverulent precipitate at the bottom of the vessel containing the acid mixture, whence it is removed and thoroughly cleansed from all traces of acidity.

If, as in the case of cellulose, we assume that starch is a condensed molecule, the formula would be a multiple of  $\text{C}_6\text{H}_{10}\text{O}_5$ , and upon this assumption other grades of nitrostarch are possible. Thus, experimentally, tetra-nitro-, penta-nitro-, and hexa-nitrostarch have been obtained, having the following compositions respectively:



Rather curiously, nitrostarch precipitated by water or

weak sulphuric acid appears to be more stable than similar compounds prepared by using the concentrated acid.

Nitrostarch seems rather liable to undergo "spontaneous decomposition," and as yet it has not been used to any considerable extent in the manufacture of explosives. It is very hygroscopic, insoluble in water and alcohol, but dissolves readily in a mixture of ether and alcohol, and in acetic ether, and also in nitroglycerine. The ignition-point of nitrostarch varies from  $155^{\circ}$  C. to  $175^{\circ}$  C., according to its composition.

Having almost the same chemical composition as cellulose, the glucoses and saccharoses have been experimented with as substances capable of nitration with the possible production of nitro-explosives. Thus, nitroglucose, nitrosaccharose, nitrolactose, and nitromannite (the latter derived from the hexatomic alcohol, mannite or mannitol) have been obtained, but as yet none of these products have proven of practical value.



## LECTURE XII.

### MANUFACTURE OF GUNCOTTON AT THE U. S. NAVAL TORPEDO STATION.

THE cotton used at this station is the kind known as "weaver's" or "cop" waste. It is the tangled clippings from the spinning-room, and is received in bales containing about 500 pounds each. This form of cotton is preferred to cotton "wool" on the ground that the thready form prevents the material from packing closely together when wet by the alkaline solutions, water, or acids used in the various processes through which it is passed, and thus permits of more complete, uniform, and speedy treatment, while it diminishes the chances of fuming during "dipping." Besides the original cost of the waste is less than that of cotton of a marketable length. The waste as received contains knots, "cops" (small bits of paper upon which the thread is wound), dirt and oil from the machines, together with incrusting substances naturally existing on the fibres, and hygroscopic moisture all of which must be removed before the material is subjected to the nitrating process. Hence the first step is the manual sorting of the waste to remove the larger foreign bodies, such as nails, pebbles, bits of wood, metal, and paper, which are sometimes found in it, and then the waste passes to the

**First Boiling-tub.**—This is a covered tub which is heated by live steam. The tub is made of white pine and has a capacity of 500 gallons. Two hundred (200) pounds of cotton are placed in the tub, to which 250 gallons of water and 35

pounds of caustic soda are added, the steam is turned on, and the whole maintained at the boiling-point for eight hours. The liquid is then drained off from the cotton, which remains thus overnight, when the tub is filled with clear water and the boiling continued for eight hours more and again drained overnight. By the manual picking the larger masses of foreign bodies have been removed. By the boiling with alkali the oils are saponified, and the soap formed acts as a detergent and removes much of the dirt, while the boiling alkaline solution acts also as a solvent for the incrusting matter. This process affects the fibre, for by prolonging the boiling with the alkaline solution or increasing the amount of alkali the fibre is materially weakened, and advantage may be taken of this to facilitate the operation of pulping, but the gain in this direction does not compensate for the loss in the product, while the hot, strong alkali solution rapidly destroys the tub.

From the first boiling-tub the wet cotton passes to the

**First Centrifugal Washer.**—This is a machine of the ordinary form and construction, being 26 inches in diameter,  $\frac{1}{4}$ -inch mesh, and making about 1400 revolutions per minute. From 6 to 7 pounds of the cotton are put in the centrifugal at a charge, the wringer is set in revolution, and a stream of fresh water is turned on the cotton and allowed to play upon it until the slippery feeling (due to the alkali) has disappeared. This operation requires about eight minutes, and the washing of the whole charge from the boiling-tub requires two hours. From here the cotton passes to the

**First Drying-room.**—This is a room 5 feet 10 inches by 11 feet 4 inches and 11 feet high, the walls and ceilings of which are sheathed with asbestos paper. Around two sides of this room are nine rows of shelves or racks made of galvanized iron wire netting 1- to  $\frac{1}{2}$ -inch mesh. Hot air enters the room from the final drier through a flue in one side and near the floor, which, after passing about and through the cotton on the shelves, issues by a ventilating flue at the top of the room. By the aid of the hot air the temperature of this drying-room is maintained at about 187° F.

The cotton from the wringer is spread on the shelves in a layer about 2 to 4 inches thick, and it remains in this room, being turned every day, after the second day, until it is perfectly dry to the touch. The time for drying varies from three to five days.

From the drying-room the cotton passes to the

**Picker.**—This is the ordinary machine used in cotton-mills, and consists of an endless flexible table upon which the cotton is fed, two small horizontal cylinders, armed with teeth, rotating in opposite directions, and a large wooden drum which is also armed with teeth. As has been said, the cotton waste as received is badly tangled and contains many knots and rolls. It can be readily understood that the stirring and boiling, produced by the live steam in the boiling-tub, tends to tangle the mass still more. The complete conversion of the cellulose depends to a large degree upon the form of the cotton when it goes into the acid. If knots and rolls be present in the cotton they produce more or less “firing,” and they are more or less yellow after the conversion. The picker serves to straighten out the tangled mass and open up the knots and rolls, so that the acid may have ready access to the fibre, but the cylinders of the picker should be so adjusted that the thread is not torn apart by this process. It takes about two hours to pass 200 pounds of cotton through the picker, and it results in about 3 pounds of loss. The cotton passes from the picker to the

**Final Drying-closet.**—This consists of a large closet 6 feet  $7\frac{1}{2}$  inches long, 4 feet wide, and 5 feet  $4\frac{1}{2}$  inches high, made of galvanized iron, which contains two sets of six drawers, each 2 feet wide, 3 feet 10 inches long, and 4 inches deep, made of the same material, with the exception of the bottoms, which are made of galvanized iron wire netting of  $\frac{1}{2}$ -to 1-inch mesh. These drawers are 5 inches apart vertically with a sheet of  $\frac{1}{4}$ -inch galvanized iron between them which serves to deflect the current of heated air. Air which has been drawn over a steam radiator is driven into this closet by means of a No. 4 Sturtevant blower, and led about and



through the cotton out of the drying-room. By means of this hot air the temperature of the closet is maintained at about 225° F., but has varied from 200° to 260° F. The cotton from the picker, which contains from 6 to 10 per cent of moisture, as all atmospherically dry cotton does, is spread over the drawers in a layer about 4 inches thick, and the drawers are then closed. The cotton is allowed to remain in the drying-closet for eight hours, at the end of which time it is estimated to contain from .25 to .50 per cent of moisture. *One half of one per cent is the largest amount of moisture which the cotton may contain at the time of dipping.* With a large amount, even if it only reaches to one per cent, a reaction takes place by which unstable compounds are formed which are not removed by the subsequent treatment which the guncotton undergoes. It is stated that an amount of moisture which is seriously objectionable when present in the cotton at the time of dipping it in the acids may be present in the acids in which the cotton is dipped without material harm to the process or product. In order that the highest nitric ester may be obtained, it is essential that the cotton at the time of dipping should be pure, dry, and cool. Hence, in order to cool it out of contact with the air, it is packed directly from the drawers of the final drying-closet, and while yet hot into service powder-tanks, the covers of which are screwed on air-tight, and then the whole is allowed to stand in a cool room overnight. The 150-pound powder-tank holds about ten pounds of cotton when filled by hand-pressure. The tanks containing the cool cotton are then transported by tram-cars running through the factory to the

**Dipping- or Converting-room.**—This room contains the dipping-troughs, acid-reservoirs, digestion-pots, and cooling-troughs.

**Dipping-troughs.**—Five of these, each having a capacity for about 150 pounds of mixed acids, are used. They are made of cast iron, and are set in an iron trough in which cold water circulates, which serves to keep the acid below 70° F. during the process of conversion. At the rear and top of

each trough is an iron shelf or grating, upon which the partially converted cotton is squeezed, and above this is an iron rod to which a hook in the end of the lever-press is attached during the process of squeezing. Only four of the troughs are used for dipping the cotton in, the first being used as a reservoir for acid for immediate consumption. The troughs are placed side by side under a wooden hood, and a flue in the rear of this hood leads the acid fumes evolved into a vacuum-chamber at the rear which connects with the suction-pipe of the ventilating-fan that ejects the fumes through a flue in the roof of the factory.

**Acids.**—The acids employed in the manufacture are purchased according to the following specifications:

The mixed acid to consist of one part by weight of nitric acid to three parts by weight of sulphuric acid. The nitric acid must have a real specific gravity of 1.5, at a temperature of 15° C., and be free from chlorine and its compounds. The color must not be darker than straw. The acid must not contain sulphuric acid in sufficient quantities to perceptibly raise the specific gravity. The sulphuric acid must have a real specific gravity of not less than 1.845, and be clear and colorless. The acids are delivered in wrought-iron cylindrical drums 3 feet 3 inches long, 28 inches in diameter, and 1 inch thick, and each holding about 1200 pounds of mixed acids. With the present knowledge of mixed acids there is no certain method of inspection except by the chemist from the station making an examination of the separate acids at the acid works before the acids are mixed, and then supervising the mixing. By thoroughly studying the question means will undoubtedly be discovered for determining whether or not the mixed acids conform to the specifications, but this has not yet been accomplished. A preliminary investigation has, however, shown that the specific gravity of the mixed acids is not the mean specific gravity of the components, and that a contraction in volume has taken place. The examination is complicated by the fact that the acid as received contains a white, finely divided solid in suspension which does

not settle completely until standing for two weeks or more. To remove it by filtration is in the nature of things a difficult operation. This suspended solid appears to be a basic sulphate of iron resulting from the slight action of the acids on the metal of the drums. Notwithstanding this action these drums offer the cheapest, safest, and altogether the most practical means of transporting the acids. Before their use the separate acids were transported to the station in glass or acid-proof stoneware carboys and mixed when desired for use. While this method gave a better check on the quality of acid delivered, the serious fires and accidents which resulted from breakage during transportation led to its abandonment. The acid from the drums is pumped into large acid-proof stoneware reservoirs in the dipping-room, and from there it is led by a conductor into the dipping-troughs.

**Dipping the Cotton.**—The cotton is weighed out in one-pound lots. Each lot is then divided into three nearly equal parts, which are successively and rapidly worked into the acids in the dipping-trough by means of the steel fork, the separate portions being well stirred about in the acid to prevent any local rise in temperature. When the whole is immersed a 10-minute sand-glass is turned and the “dipper” passes on to the next trough, where this operation is repeated. By the time he has filled the fourth trough with its charge the sand has run its course above the first trough, so this charge is withdrawn from the acid, placed upon the grating, squeezed by the lever-press as completely as possible and then placed in the digestion-pot.

**The Lever-press** is an iron bar about 5 feet long, having a hook at one end. A plate is attached to the bar by a pivot about 8 inches from the hook. To use the press the hook is attached to the rod above the dipping-trough, the plate is placed on the cotton, and pressure is applied to the longer end of the lever.

**Digestion-pot.**—This is an ordinary two-gallon crock made of coarse stoneware, glazed inside and out, and provided with a cover. It is of the first importance that the



pot should be sound and the glaze intact so that no leaking can take place, for if moisture should reach the charge in the crock the latter would be "fired." Immediately before use the pots are wiped out with a little acid so as to remove any moisture which may have accumulated or condensed on their walls. This process is technically known as "drying-out." The mass of partially converted cotton saturated with acid weighs, as placed in the pot, from 10 to 12 pounds. When it is put in the pot it is squeezed down compactly by means of a hand-press, and the pot is then covered and placed in water in the cooling-trough, where it remains overnight. A gang of two men can thus treat 100 pounds of cotton in a working day of 8 hours.

**Cooling-troughs.** — These are made of wood 2 inches thick, are rectangular in shape, are lined with lead and provided with a water-tap at one end and an overflow-pipe at the other. The latter pipe is just high enough and of such size as to prevent the water in the trough from rising above the level of the acid and guncotton in the pots. The troughs are 1 foot 5 inches wide,  $8\frac{1}{2}$  inches deep, and 24 feet 6 inches long. Each one will hold 20 pots. Six are used, and one is reserved for emergencies. Cold water is kept circulating through these troughs in summer, but in winter they are simply filled with water. From the cooling-troughs the guncotton passes to the

**Acid-wringer.** — This is a centrifugal wringer made of mild steel and provided with a cover to prevent the acid or acid fumes from escaping. The wringer is 20 inches in diameter and 9 inches deep, has a  $\frac{1}{8}$ -inch mesh, and makes 1400 revolutions per minute. It is provided with a flue leading to a ventilating-fan by which the fumes are driven into the outer atmosphere, while a pipe from the bottom leads the extracted acid in a receiver in the factory cellar. Before using for the day this wringer is "dried out" by pouring in a pitcherful of acid and rotating the basket. Two pots full of guncotton are wrung at one operation, and this occupies from three to four minutes. The operation should

be conducted with caution, and extreme care should be taken that no moisture or oil reaches the mass. As the digestion-pots have been immersed in water in the cooling-troughs, it is necessary to let them drain and to dry their outer surface before taking them to the acid-wringer. Several explosions or "firings" which have taken place in wringers have been traced to drops of oil from the machinery, or of perspiration from the faces of the workmen, which have fallen on the guncotton. The wrung guncotton is taken from the wringer by hand, the hands being covered with rubber gloves, and it then passes to the

**Immersion-tub.**—This is a wooden tub of 800 gallons capacity, provided with a perforated false bottom, and having a  $3\frac{1}{2}$ -inch inlet and a  $3\frac{1}{2}$ -inch outflow-pipe. At one end is a wooden drum 2 feet in diameter, provided with feathers, and placed so as to be nearly one-half immersed in the water of the tub when the tub is filled. This cylinder rotates horizontally about its axis, and serves as a beater to carry the guncotton under the water. Above the tub and at one side of the beater is placed a wooden box or hopper, lined with lead, which is provided with a door in the side, through which the guncotton is introduced into the hopper, and a slot in the bottom by which the guncotton is fed to the tub. The object of the immersion process is to wash out the greater portion of acid from the guncotton. As stated above, a small quantity of water is likely to cause "firing"; hence, to effect this washing successfully, it is necessary to use very small portions of guncotton at a time, to use very large quantities of water so as to drown the guncotton, and to perform the operation so quickly that the acid is removed from the guncotton and distributed through the great body of water before any local heating can take place. This is effected as follows: The tub being filled with water, the water flowing at full speed, and the beater being in rotation, two crocks of wrung guncotton are placed in the hopper. Then the workman inserts his hand, protected by a rubber glove, and little by little pushes the guncotton through the

slot, and this operation is repeated until fifty crocks are fed into the tub. When well washed the guncotton is placed in a wooden rack to drain. Owing to the scarcity of fresh water at the torpedo-station salt water is used in the immersion-tub, so the guncotton from the tub is wrung out in a centrifugal wringer, and washed with fresh water until the salty taste has disappeared. Two crockfuls are wrung at a time, and three washings are generally sufficient. No matter how much the guncotton is washed in cold water, it still retains acids or easily decomposed material, which can only be removed by boiling; hence from the immersion-tub the guncotton passes to the

**Second or Guncotton Boiling-tub.**—This consists of a wooden tub of 300 gallons capacity, which is provided with a perforated false bottom and heated by a steam-coil. The inlet-pipe and coil are cut off from the interior of the tub so that the metal cannot come in contact with the guncotton. Here fifty pots of guncotton are boiled for eight hours in fresh water to which 10 pounds of carbonate of soda have been added, then drained overnight, washed with fresh water in a centrifugal wringer, returned to the boiling-tub, boiled with fresh water for eight hours, again drained overnight and again washed with fresh water in the centrifugal. The guncotton next passes to the

**Pulper.**—This machine is the ordinary “beater,” “rag-engine,” or Hollander,” used in paper-mills, and consists of a wooden tub 12 feet long, 5 feet wide, and 2 feet deep, with curved ends. The tub is partially divided along its longer axis by a wooden partition (of the same height as the walls of the tub) into two parts—the “working side,” in which the guncotton is shredded between the knife-edges on the revolving cylinder and those on the “craw,” and the “running side,” into which the shredded material is thrown by the revolving cylinder. The revolving cylinder is of wood, is 28 inches in diameter, 28 inches long, carries forty crucible-steel knives, and rotates two hundred times a minute. Under the cylinder is a massive oak block, called the “craw,” the concave



surface of which equals one fourth the circumference of the cylinder. The side of the block leading to the curved face is gently inclined, while on the side beyond the curved face it is sharply inclined. In the centre of the craw below the revolving cylinder is fitted a box of steel knives, and the cylinder is so adjusted by set-screws attached to the socket in which its shaft revolves that its knives just clear the bundle of knives in the craw. The cylinder is enclosed in a wooden cover, extending nearly the length of the partition, to prevent loss of the material by centrifugal action. From 300 to 350 pounds of guncotton are slowly fed into the pulper, and water is added until, when the cylinder is revolving, the mass just reaches the top of the tub to the right of the cylinder. During the feeding the guncotton is held in a wall-pocket made of thin boards and canvas, which is placed at the left-hand end of the pulper. When the cylinder is set in revolution the guncotton is drawn between the knives and shredded and the paste forced over the craw, where, as it flows sluggishly, it is heaped higher than at the other end of the tub, but it generally flows to the other end, is drawn again between the knives, and so it continues until the whole of the guncotton is cut to the fineness of corn meal. When the pulper is in good working order this operation takes two days for a charge of the size stated above. The mass is then run off into the

**Poacher.**—This is a wooden tub similar in form to the pulper, but the cylinder is armed with wooden feathers instead of knives, and it serves simply to keep the guncotton in suspension in the water and to keep the whole in mass in rotation about the tub. The poacher has a capacity of about 900 gallons. When the pulp has reached the poacher the guncotton is allowed to settle, and the water is drained off by means of a telescopic overflow-pipe in one end of the poacher. The tub is filled with fresh water, the cylinder set in revolution, and the circulation kept up for one hour, when the settling and draining is repeated, and these operations are continued for two days, making about six washings and settlings, when a sample is drawn and tested. If the sample fails to pass the

test the washing in the poacher is continued until the guncotton will pass. When thoroughly washed the guncotton is again drained, 3 pounds of precipitated chalk, 3 pounds of caustic soda, 300 gallons of lime-water, and sufficient water to make the whole up to about 800 gallons, are added to it, and the whole is sucked up by means of a vacuum-pump into the

**Stuff-chest.**—This is a cylindrical iron vessel of about 850 gallons capacity, fitted with a manhole at the top, which is closed by an air-tight cover, and provided at the bottom with an inlet-pipe through which the pulp enters, and an outlet-pipe through which the pulp is delivered. Through the centre of the tank is a vertical shaft, which is provided with four feathers, and which is geared to a horizontal shaft above it. The object of this stirrer is to keep the guncotton and other solids uniformly suspended in the liquid so that the same proportions of each, as nearly as possible, may be delivered to the moulding-press. The stirrer is run for about twenty minutes before the moulding begins, and is kept in operation until the moulding ceases. The stuff-chest rests upon stringers at the top of the factory so that its contents may gravitate to the press. The pulp first goes, however, to the

**Wagon,** which is a cylindrical copper vessel of about 25 gallons capacity, suspended by rollers upon a railway so that the top of the vessel just clears the outlet-pipe of the stuff-chest, while the bottom is well clear of the top of the moulding-press. Inside the wagon is a vertical stirrer, similar to that in the stuff-chest and playing the same part, which is geared to a horizontal shaft that rotates between the rails. The pulp is delivered by an orifice in the bottom, which is closed by a valve which moves vertically and is operated by a lever and cord at the top of the wagon. A one-inch rubber tube one foot long is attached to the outlet of the wagon so as to assist in delivering the pulp at the desired point. The wagon is filled by rolling it under the stuff-chest and opening the valve in the outlet-pipe of the latter. The stirrer then being in rotation, the wagon is rolled along until it reaches the moulding-

press, when the rubber tube is led successively to each compartment of the moulding-press, the lever is pulled, and the press is loaded. One wagon-load serves for about three charges for the moulding-press.

**Moulding-press.**—This is a hydraulic press made of bronze and containing four rectangular compartments 2.8 inches square with chamfered corners. The press is closed by a block which is hinged at the back and locked at the front by a lever clamp swivelled eccentrically. The pistons have a 28-inch stroke. Through the centre of each piston-head is a rod  $1\frac{1}{2}$  inches in diameter, which is screwed in the base of the press and reaches quite to the top, and which is used as the core to form the detonator hole in the guncotton block. The top of each compartment is closed by a plate perforated with holes, through which the water which is squeezed out of the pulp escapes and flows into the reservoir between the compartments. The finished guncotton block is 2.9 inches in diameter,  $3\frac{7}{8}$  inches in diagonal (the corners being chamfered), and 2 inches in height, and to produce this it is necessary that the moulded block should be 2.8 inches in diameter, and  $5\frac{1}{4}$  to  $5\frac{1}{2}$  inches high, when the moulding pressure is 100 pounds to the square inch. Knowing the size of the compressed block desired, it is determined by experiment how much of the pulp is necessary to produce it, the length of the stroke of the piston being increased or decreased to produce this result. The pistons having been set, by means of the rod in the centre of the piston-heads, the pulp is run in until the compartment is filled, and this is repeated with each of the four compartments. The perforated plates are inserted, the cover closed and locked, and the pressure applied. The pressing occupies four minutes. When primers (smaller disks or blocks) are desired only one fourth the quantity of pulp is taken, and the moulded blocks have but one fourth the height of the service-blocks.

**Final Press.**—This press is a Sellers hydraulic press, made of steel, with an 18-inch ram. On the head of the ram are nine pistons which fit neatly into nine apertures in the



press-block above them. The press-block is made of gun-bronze, and it is 15 inches wide, 22 inches long, and 7 inches thick. It is supported in place by being bolted to the vertical columns which support the head of the press. Above the press-block is a travelling-block, which is hung by rollers on a horizontal track, so that it may be brought in contact with the top of the press-block, or pushed off from it at will. Two perforated steel plates which neatly fit the aperture, one, which is  $\frac{1}{3}\frac{1}{2}$  inch thick, above, and one, which is one inch thick, below the guncotton block, and these diaphragms serve to distribute the pressure uniformly over the surface of the blocks, while the perforations allow the water which is squeezed from the block to escape. The upper plate also bears on its lower surface the marks which it is desired to impress on the block, and thus serves as a die to stamp the guncotton.

A very detailed account of the history of each charge is kept in the factory, and the system of marking enables those in charge to keep track of each charge until it is expended.

The press is loaded by rolling off the travelling-block, lowering the pistons, dropping in the lower plates, then the moulded guncotton blocks, then the upper plates, and, finally, rolling the travelling-block back into place again. The pressure is then applied by means of a powerful hydraulic pump in a pit beside the press, the safety-valve of which is set to discharge at from 1800 to 2000 pounds as indicated by the pressure-gauge. Of course the total effect of the ram will be transmitted to the pistons, and, as the area of the head of the ram is to that of the nine pistons' head as 3.4 : 1, the pressure per square inch on the guncotton will be 6120 pounds when the initial pressure is 1800 and 6800 pounds, when the initial pressure is 2000. The pressure reaches the maximum about three minutes after the pump is set in operation, and this pressure is maintained for about one minute by the sand-glass. When the ram is released the travelling-block is rolled off, the pump is set at work again, and the finished blocks of guncotton are pushed to the surface of the press-block. When priming-blocks are to be pressed, four of the moulded blocks

are inserted in each of the compartments of the press-block, and they issue firmly compacted together, but showing distinctly the marks of demarcation of each of the moulded blocks, and they may be readily split apart along these lines. When the guncotton is taken from the final press it contains from 12 to 16 per cent of moisture. It is but natural to apprehend danger from subjecting guncotton which is so nearly dry to the high pressures which are employed, especially when we consider that small particles of the substances might get pinched between the metal parts, and that some of these might be air-dried while the press is idle. It has been reported that such explosions have occurred in this way abroad, but it has been impossible to verify these reports.

However, no such explosions have thus far occurred at the torpedo station, though the press-block was once split open. As far as could be ascertained, this was due to the workman's having inadvertently inserted three of the perforated plates into one compartment and only one into another, thus causing the whole force of the ram to be exerted on one piston, which bent and jammed and finally split the block. The guncotton from this pressing was recovered intact from the press-block. To guard against serious results following an explosion at the station, the press is surrounded by a rope mantlet (such as was used in monitor turrets during the war of the rebellion), which is braided from Manilla rope  $1\frac{1}{2}$  inches in diameter. There are four thicknesses to the mantlet, and this can be relied upon to arrest pieces of the metal if projected with not too great velocity. When the guncotton blocks are taken from the press they are two inches in height, but after standing awhile they swell a little. Though when taken out they contain but from 12 to 16 per cent of water, as sent into the service they contain about 35 per cent. This is added by allowing the blocks to soak in a trough of fresh water until they cease to absorb water.

**Storage of Guncotton.**—The blocks are packed in the torpedo-cases at the guncotton factory as fast as they are made, the primer-cases being filled with wet primers. A suf-

ficient proportion of dry primers are sent with each outfit, and when the torpedoes are desired for use the wet priming-blocks are withdrawn from the primer-can and dry ones substituted. These wet ones are then dried by splitting the blocks apart into  $\frac{1}{2}$ -inch portions, weighing each one, stringing them on a perfectly clean brass or copper rod or tube, separating the blocks one from another, and suspending the rod in a suitable dry place (away from any direct source of heat) where they will be freely exposed to air and yet be under cover. The blocks are to be weighed separately from time to time, the weights being marked on each with a soft lead-pencil, and they are to be dried until they cease to lose weight.

NOTE ON DRYING GUNCOTTON.—With the adoption of smokeless powders, the great majority of which contain guncotton, it has become necessary to devise a safe method of drying this explosive, which under ordinary conditions of storage and transport contains about 30 per cent of moisture.

On account of its gradual decomposition when subjected to a continued temperature of  $65.5^{\circ}\text{C}.$ , it has been found to be advisable to limit the maximum temperature of the drying-house to  $46^{\circ}\text{C}.$  An additional danger, however, arises from the fact that guncotton possesses highly electrical properties, and the passage of a current of heated air over the explosive may develop sufficient electricity to fire it; in fact, several accidents which have occurred in drying this explosive have been attributed to this cause.

The most common method of drying pulverulent guncotton is to place it upon shallow copper trays, which in turn are placed upon racks in the drying-house. The warm, dry air is introduced into the room (by means of a fan or blower) near the ceiling, circulates over and between the trays, and is drawn out by means of an exhaust on a level with the floor, the outlets of both air-shafts being covered with copper gauze. The floor is covered preferably with linoleum, and is also fitted with openings covered with light gratings in which the dust which is unavoidably formed during the process of drying is collected, and from which it should be carefully removed at regular intervals.



## LECTURE XIII.

### SERVICE TESTS FOR GUNCOTTON.

THERE are several standard tests which, applied to guncotton, either during the process of manufacture or at any subsequent time to the finished product, determine its chemical character. They are as follows:

1. Determination of moisture in guncotton
2. Determination of ash of guncotton.
3. Test for the presence of free acid.
4. Heat or stability test.
5. Nitrogen test.
6. Solubility test.
7. Determination of unconverted cotton.
8. Determination of alkaline substances.
9. Determination of temperature of ignition.

Of these tests but two—the stability and solubility—are applied during the process of manufacture.

#### **Preparation of Unfinished Guncotton for Testing.—**

Before applying the test the guncotton must be carefully prepared beforehand. In case of the unfinished guncotton, about one quart of the pulp is taken from the poacher after having been subjected to about six washings. As it is of the greatest importance that the sample tested should represent the average composition of the charge in the poacher, it is drawn in very small quantities at a time, while the revolving cylinder is in operation, and the pulp is circulating actively, portions being taken from both top and bottom.

The sample is allowed to stand until the guncotton has

settled, when the water is poured off, and then one half of the guncotton is wrapped in a thoroughly clean linen cloth and placed under a hand-press, where it is subjected to a tolerably severe pressure for about three minutes, or until water ceases to flow from it.

The mass is then taken out in the form of a cake, which is broken up into fine particles and rubbed between the hands. About 13 gm. (or 200 gr.) of the guncotton thus comminuted are placed in a paper tray, which is placed on top of a water-oven heated up to 120° F., care being taken that the tray does not come into contact with the walls of the oven. The mass is thus heated, with constant stirring, for fifteen minutes. When perfectly dry the sample is transferred to a covered glass funnel with roughened sides, the neck of which is connected with a bellows through an ordinary aspirator bottle. The mouth of the funnel is covered with a piece of clean muslin, and by means of the bellows the finest particles of the guncotton are blown on the sides of the funnel, from which they are carefully removed. After these particles have been exposed to the atmosphere of a normally dry and warm room for about two hours the sample is ready for testing.

**Preparation of Finished Guncotton for Testing.**—For these same tests—stability and solubility—the finished guncotton must be prepared in a manner similar to that just described for the pulp. A disk or block of guncotton is split, and then by gentle scraping or rasping about 40 grammes (or 600 grains) are removed from the centre of the mass. This is placed in a litre flask and a half-litre of distilled water at a temperature of 39° C. poured upon it, when the flask is corked and shaken vigorously two or three minutes. The contents of the flask are then filtered through muslin, and then, wrapped in the filter, are subjected to a moderate pressure in a hand-press. This operation is repeated three times, when the sample is dried and the rest of the preparation is in all respects precisely the same as that described for the pulp.

**Determination of Moisture in Guncotton.**—The amount of moisture in guncotton is readily determined by weighing

carefully two grammes of the cotton as it is scraped from the disk or block in a watch-crystal, and placing it in an oven at  $40^{\circ}$  C. for twelve hours, at the end of which time it is placed in a desiccator over sulphuric acid and dried to constant weight. The loss of weight gives the moisture, whence the percentage of moisture is calculated.

**Determination of Ash of Guncotton.**—This may be done as follows: Melt a little pure paraffin in a weighed crucible (porcelain or platinum) by gentle heat, and add a known weight (2 grammes) of the sample. Ignite the mixture from above, and when all is consumed ignite the crucible over a lamp, and then allow it to cool and reweigh. The increase in weight gives the ash.

The mixture must be ignited from above, and at as low a temperature as possible, to prevent the mass from being thrown out by an explosion. An incandescent platinum wire may be used to ignite the mass in the crucible.

After as complete incineration as possible over a lamp or Bunsen burner, the ash should be moistened with a solution of ammonium carbonate, and reignited several times at  $200^{\circ}$  C. to constant weight.

The increase in the weight of the crucible gives the weight of ash.

**Test for the Presence of Free Acid.**—Put about one gramme of the cotton scraped from the disk in a test-tube (25 c.c.), half fill the tube with distilled water, cork the tube or close it with the thumb, and shake vigorously for a few minutes. Allow the cotton to settle, and test the supernatant water with litmus paper, or, better, with methyl-orange. Should free acid in considerable quantity be found, the subsequent tests are unnecessary, except as additional proofs of the unsafe condition of the guncotton.

**Heat or Stability Test.**—The causes of the decomposition of guncotton have already been alluded to, as well as the unstable and dangerous condition of the explosive during the decomposing stage. The object of the heat-test is to determine the exact character of the guncotton at any time as



regards its stability. The test itself depends upon the principle that *when potassium iodide is decomposed in the presence of starch, the iodine is liberated and reacts with the starch to form a colored body*. This decomposition of potassium iodide is effected by the oxides of nitrogen and nitrogen acids, and in this test the heat of the bath drives off any free acids present in the guncotton, or decomposes any unstable bodies, and liberates the nitrogen oxides or acids, which react on the test-paper, producing the color referred to. As this test is applicable to all explosives containing the nitrogen oxides or acids, it will be described at length.

**Apparatus and Materials required for the Heat-test.**

—1. *Water-bath*.—This consists of a glass globe about eight inches in diameter, which is filled with water to within a quarter inch of the top when the water is heated. The globe is open at the top, and the mouth is closed by a copper plate, which is perforated with a small hole in the centre to receive the thermometer, and with several holes about the central one of slightly larger diameter than that of the test-tubes. Around each of these holes and attached to the under face of the cover are four spring-clips inclined toward each other, so that when the test-tubes are inserted in the holes the clips close firmly about them and hold them in any desired position. The globe is placed on strips of wood in a metallic vessel about ten inches in diameter, and both globe and bowl are then filled with water. This outside bowl enables us to readily heat the apparatus without the danger of breaking the glass globe, while the large quantity of water is of material assistance in keeping the temperature constant for a considerable period of time.

2. *Temperature Regulator and Thermometer*.—In making the test it is of the greatest importance that during the entire time that the test-tubes containing the sample are immersed, the temperature should remain perfectly constant. Wherever gas is available for heating purposes in the laboratory, this is easily managed by means of a thermostat. When gas is not at hand, by careful attention to the flame of

either an oil-stove or spirit-lamp the temperature can be regulated during the test. The temperature is noted by means of an accurate thermometer introduced into the bath through the central hole in the cover of the globe.

3. *Test-tubes*.—The test-tubes should be from 12 to 14 cm. long, and of such diameter that each will hold from 20 to 22 c.c. of water when filled to the height of 5 inches. They should be marked with a ring, drawn around them with a diamond,  $2\frac{1}{2}$  inches from the bottom, and the explosive should be compressed to this mark. Clean glass rods are used for pressing the guncotton in the tubes. They should be provided with flat heads, and be long enough to reach easily to the bottom of the tubes.

4. *Test-paper Holders*.—These consist of small glass rods about 20 cm. long, having a piece of platinum wire about one centimetre long fused into one end and bent into a hook. These rods pass loosely through holes in taper corks which fit neatly in the mouths of the test-tubes.

5. *Test-papers*.—The test-paper used is known as *starch and potassium iodide* paper, and is made as follows: Forty-five grains of white starch, which has been well washed in cold distilled water and thoroughly dried, are added to  $8\frac{1}{2}$  ounces of distilled water, and the whole is heated to boiling, with constant stirring, and is kept gently boiling for ten minutes. Fifteen grains of pure potassium iodide (i.e., KI, which has been recrystallized from alcohol) is now dissolved in  $8\frac{1}{2}$  ounces of distilled water, and the two solutions are mixed and allowed to cool. Strips or sheets of fine white filter-paper, which have been previously washed in distilled water and redried, are dipped in the above solution and allowed to remain in it for not less than ten seconds, when they are removed and hung up to dry in a warm, dark room which is free from laboratory dust and fumes. When dry, the upper and lower margins of the strips or sheets are cut off and the paper is preserved in well-stoppered, dark-colored bottles, or in ordinary bottles which are kept out of contact with the direct rays of light. For use in making the test, the paper is cut into small rec-

tangular pieces, 10 mm. by 20 mm. (about  $\frac{4}{10}$  by  $\frac{8}{10}$  of an inch). They are attached to the test-paper holders by piercing them near the top with the point of a knife, two incisions being made at right angles to each other forming a cross. The point of the platinum wire is inserted through the centre of the cross, and the hook is bent firmly together so as to hold the papers rigidly in line with the rod of the holder.

6. *Glycerine Solution*.—This is made by dissolving ten per cent of pure glycerine in distilled water. It is kept in a small flask, the mouth of which is closed by a cork, and the latter is perforated to receive a small glass rod which is long enough to reach the bottom of the flask, and drawn to a point at its lower end. The glycerine solution is used to moisten the test paper, and is applied by holding the test-paper holder vertically with the paper uppermost, and then touching the paper at the edge where it is fastened to the platinum hook, with the rod just as it is drawn from the solution. Enough solution is applied to thoroughly moisten the paper across its entire width and for one half its length. The holder is held with the paper upward until the solution has been drawn by capillarity up to the middle of the paper, and is found to go no further.

7. *Standard Tint-paper*.—As in all tests depending upon a comparison or determination of color considerable difficulty is encountered practically in conducting the heat test, especially by inexperienced operators. And since it is of the greatest importance that the exact moment at which the coloration upon the test-paper reaches the proper depth or shade should be noted, a standard tint-paper has been devised to aid observers in this determination.

It is prepared by making a caramel solution in distilled water of such concentration that when diluted one hundred times (10 c.c. made up to a litre) the tint of the solution equals that produced by the Nessler test (2 c.c.) in 100 c.c. of water containing 0.000075 gramme of ammonia, or 0.00023505 gramme of ammonium chloride. With this solu-



tion lines are drawn on slips of white filter-paper by means of a clean quill pen. When the slips are dry they are cut into pieces of the same size as the test-papers, and in such a way that each piece has a brown line across it near the middle of its length, and only those strips are preserved in which the brown line has a breadth varying from  $\frac{1}{2}$  to 1 mm. ( $\frac{1}{25}$  to  $\frac{1}{50}$  of an inch). This may be used by hanging a strip in a test-tube beside the tube in which the test is being made, and noting each until a brown (or yellow) line appears on the test-paper, similar in depth or shade to that in the standard tint-paper. I consider the use of standard tint-paper of doubtful value, the only true and reliable guide being experience.

**How to Make the Heat Test.**—Insert the thermometer in the bath to a depth of about three inches, and apply the heat until the temperature is constant at  $65^{\circ}.5$  C. ( $150^{\circ}$  F.). The weighed sample of guncotton (20 grains) is introduced into the tube and pressed down by means of the glass rod to the mark, and the tube is closed with a loosely-fitting cork. The tube is then inserted in the bath until the upper surface of the sample coincides with the level of the water, *and the exact time of insertion is noted.* The test-paper is *now* moistened with the glycerine solution, the paper being drawn up close to the bottom of the cork. The holder with the test-paper attached is substituted for the cork in the test-tube. Shortly after the test-tube has been introduced into the bath, a ring of moisture will begin to form in the upper part of the tube. As soon as this is observed, the test-paper is lowered by pushing the rod through the cork until the *line of demarcation between the wet and dry portions of the paper is coincident with the lower edge of the ring of moisture.* The test-paper is now closely watched, and *as soon as the faintest sign of discoloration appears on the test-paper* (and it appears at the line of demarcation between the wet and dry portions), *the time is again noted.* When the standard tint-paper is used, the second time is taken when the two colors (that on the test-paper and that on the standard tint-paper) are of precisely the same depth or shade.



The time elapsed for stable guncotton must not be less than *fifteen* (15) *minutes*. In the U. S. Artillery School Laboratory it is customary to make three tests of each sample at the same time, using as many tubes, and introducing them in rapid succession, so that the conditions may be practically the same and the mean of the three tests is taken. The record is kept as follows:

U. S. ARTILLERY SCHOOL,  
DEPARTMENT OF CHEMISTRY AND EXPLOSIVES,  
January 23, 1890.

#### HEAT TEST OF GUNCOTTON.

*Sample:* Torpedo Station, Charge 100, 1889.

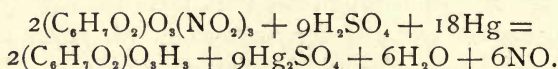
	1.	2.	3.
Time of stopping.....	10.51	10.53	10.55
Time of starting.....	10.30	10.33	10.38
Time elapsed.....	21	20	17
Mean.....	19 m. 20 s.		

Condition of sample : *Stable*.

.....

.... *Lieutenant*, .... *U. S. Artillery*,  
*Operator.*

**Nitrogen Test.**—This test depends upon the principle that *when cellulose nitrates are treated with pure concentrated sulphuric acid in the presence of mercury, they are decomposed, all of the nitrogen being evolved in the form of nitrogen oxides*, which may be collected and measured, whence the percentage of nitrogen may be easily calculated. Should the nitrate under examination be the tri-nitrocellulose, the reaction would be represented as follows:



Similar equations may be written to represent the reactions which occur in the cases of the other nitrates, and from the percentage of nitrogen found we are able to decide very approximately the particular nitrate, the presence of which is the cause of trouble.

The test is easily made by means of a nitrometer, the form used in the Artillery School Laboratory being that de-

vised by Bunté for gas analysis. This apparatus consists of two glass tubes of about 150 c.c. capacity, connected at their lower ends by means of a rubber tube. The upper end of one of the tubes is fitted with a thistle-bulb funnel, between which and the tube proper is a three-way stop-cock; there is also an ordinary stop-cock fitted at the lower end of this tube. This tube, which is called the burette, is graduated into tenths of cubic centimetres, while the other tube, called the filling tube, is ungraduated. Both tubes are mounted in a burette-holder so as to be vertical and side by side, but either may be raised or lowered at will. To conduct the test, the nitrometer is first filled as follows: The rubber tube having been securely attached, the graduated tube is firmly clamped in the burette-holder and both stop-cocks opened; then, holding the plain tube in the left hand so that it is raised about two thirds of its length above the graduated one, pour into the nitrometer through a funnel fitted in the plane tube enough mercury to completely fill the graduated tube and partially fill the plain one. Then close the upper stop-cock of the graduated tube and secure the plain tube in the burette-holder alongside of the former and on a level with it. Next introduce into the funnel at the top of the burette 300 milligrammes of thoroughly dried, finely divided guncotton, and cover it with 5 c.c. of pure concentrated sulphuric acid. The upper stop-cock is then *very carefully* opened, and the mixture is swept into the tube, additional acid being added to wash every particle of the guncotton into the tube. *It requires the most careful manipulation at this point in order that the flow of acid may be constant and that no air gets into or gases escape from the tube,* in either of which events the results are vitiated.

It is well to have an excess of acid so that the stop-cock may be closed before the last traces of the acid run into tube. The reaction begins as soon as the mixture reaches the mercury, and is assisted from time to time by closing the lower stop-cock of the burette, removing it from its clamp and shaking it carefully. After the reaction has entirely ceased



(usually at the end of one-half hour), the tubes are adjusted so that the mercury in each is at the same height, and the exact amount of acid in the burette noted. The filling-tube is then raised so that the level of the mercury in it is higher than that in the burette by one seventh of the number of divisions in the burette occupied by the sulphuric acid and *the volume of the gas is read off*. The tubes are again placed side by side, and allowed to stand for fifteen minutes, when the volume of gas is verified by adjusting the tubes as before. When the readings become constant, the thermometer and barometer are noted and the volume of the gas is reduced to 0° C. and 76 cm. by Charles' and Mariotte's laws, which may be conveniently written as follows:

$$V_t = V_0 \frac{P}{P_t} \left(1 + \frac{1}{273} t\right),$$

in which  $V_t$  represents the volume of the gas at the observed temperature;

$V_0$  represents the volume of the gas at 0° C.;

$P_t$  represents the observed pressure of the atmosphere at the time of the experiment;

$P_a$  represents the pressure of the atmosphere at 76 cm.;

$t$  represents the observed temperature at the time of the experiment.

The weight of the sample being known, from the data obtained from the methods given above, the weight of nitrogen present and the percentage in the guncotton are readily calculated according to the formula assumed to represent military guncotton. Thus, if we accept the results of Eder's investigations, and assume the formula  $(C_{12}H_4O_4)O_6(NO_2)_6$  to represent the highest degree of nitration possible, the percentage of nitrogen cannot exceed 14.14, and allowing for errors due to manipulation, etc., it should not fall below 13.665. If, on the other hand, Vieille's formula,  $(C_{24}H_{20}O_9)O_{11}(NO_2)_{11}$ , represent military guncotton, which is always

assumed to be the most highly nitrated product attainable, the highest percentage of nitrogen to be obtained cannot exceed 13.496, and, with the same allowance for personal errors of the operator, should not be less than 12.996.

**Solubility Test.**—This test depends upon the principle that *the lower cellulose nitrates are soluble in a mixture of ether and alcohol, while the tri-nitrocellulose is insoluble in such a mixture.* This test logically follows that just described exactly as the heat test follows that for the presence of free acid. By this test we determine the presence or absence of the lower or unstable nitro-compounds, and taken in connection with the nitrogen test, which will be described later, we are able to determine very closely which particular compound is the cause of trouble, and therefore the exact character of the explosive.

About 20 grammes of the pulp from the poacher, or 10 grammes of the finished product, are treated in the hand-press as described for the heat test, and the cake is then broken up and placed in an air-bath, where it is dried at a temperature of 40° C. for about two hours, being rubbed between the hands occasionally to break up the lumps. When well dried it is removed from the bath and exposed to the air for an hour. Two grammes of the sample thus prepared are weighed out in a watch-crystal and carefully introduced into a flask, and covered with four fluid ounces of a mixture of *one volume of absolute alcohol* (sp. gr. 0.805) and *two volumes of Squibbs' strongest ether* (sp. gr. 0.735). The flask is then corked and shaken at intervals for two hours. At the end of that time the contents of the flask are decanted upon a weighed linen or muslin filter (which has been previously washed in some of the ether-alcohol mixture) and washed on the filter with four ounces more of the mixture; the filter and contents are then squeezed thoroughly to remove any of the solution present. (The funnel in which the filter is placed is introduced into a perfectly clean bottle, so that the mixture may be saved for distillation and future use.) The residue in the filter is carefully removed by means of a glass spatula, and is replaced in

the flask and covered with four ounces of fresh ether-alcohol. The flask is again corked and shaken at intervals for one-half hour, and the contents are then decanted upon the same filter as before and washed with four ounces more of the ether-alcohol mixture. The filter is again squeezed, and then, with its contents, is spread upon a perfectly clean glass plate, and placed in a drying oven and heated until all odor of the alcohol has disappeared. It is then exposed to the air for two hours and weighed. The drying and exposure to the air are repeated until the weight is constant. The difference between the weight of the guncotton taken and that of the residue found gives the weight of the substance dissolved, whence the percentage is readily calculated. The soluble matter in guncotton should not exceed 10 per cent. The guncotton made at the U. S. Naval Torpedo Station contains usually less than 6 per cent.

On account of the expense, it is usual to take the mean of two tests at the U. S. Artillery School Laboratory as sufficient to establish the percentage of soluble matter, unless the discrepancy between the two is such as to render doubtful the accuracy of either result, in which case a third and possibly a fourth determination is made.

The record is kept as follows:

U. S. ARTILLERY SCHOOL,  
DEPARTMENT OF CHEMISTRY AND EXPLOSIVES,  
January 27, 1890.

#### SOLUBILITY TEST OF GUNCOTTON.

*Sample* : Torpedo Station, Charge 100, 1889.

	I.	2.
Weight of sample (in milligrammes).....	2,000	2,000
Weight of filter.....	2,955	3,008
Weight of sample and filter.....	4,955	5,008
Weight of insoluble guncotton and filter.....	4,821	4,891
Weight of soluble guncotton.....	134	117
Mean.....		125.5
Percentage of soluble guncotton.....		6.275

.....*Lieutenant* .....*U. S. Artillery,*  
*Operator.*



**Test for Unconverted Cotton.**—Besides the determination of the soluble guncotton, it is sometimes necessary to determine the amount of unconverted cellulose present. This may be done by treating the residue from the ether-alcohol washing with ethyl acetate (acetic ether). By digestion with this solvent the cellulose nitrates are dissolved, and the unconverted cellulose is left behind and may be collected on a weighed filter. Or it may be treated by boiling with a solution of sodium stannate made by adding caustic soda to a solution of stannous chloride until the precipitate at first formed is just redissolved. This solution dissolves the cellulose nitrates, but does not affect cellulose.

**Determination of Alkaline Substances.**—For certain purposes it is often desirable to know the amount of calcium and sodium compounds present in the finished guncotton. For this test five (5) grammes of air-dried guncotton are taken from the centre of a disk or block, rubbed up finely, and extracted by means of 100 c.c. of standard hydrochloric acid diluted with about twice its volume of water. The guncotton and acid are allowed to digest together for a short time, the liquid is decanted, and the guncotton washed either by decantation or upon a filter, until the washings exhibit no acid reaction. The washings are added to the decanted liquid, and 100 c.c. of standard sodium carbonate solution is poured in. The amount of sodium carbonate neutralized is determined by titrating with the standard acid solution, using litmus or methyl-orange as an indicator. The amount of alkalies in the guncotton is measured by the amount of unneutralized sodium carbonate. The standard sodium carbonate solution may be prepared by dissolving 3 grammes of the salt in 100 c.c. of distilled water, or the standard alkaline and acid solutions may be so constructed that equal volumes will neutralize each other.

**Determination of the Temperature of Ignition.**—Guncotton, when properly made, should not ignite below 180° C. To determine the point at which guncotton ignites, put about 0.05 gm. in a strong test-tube, and suspend the tube in

an oil-bath previously heated to  $100^{\circ}$  C., and gradually increase the temperature of the oil until the guncotton flashes. Note the temperature of the bath by means of a thermometer, the bulb of which is immersed in the oil. The temperature of ignition varies according as the heating is gradually or suddenly applied; and in order to determine the temperature of ignition when the guncotton is suddenly heated, an oil-bath fitted with a top containing six or more openings for test-tubes and a central hole to receive a perforated cork, through which the bulb of a thermometer projects into the oil below, may be used. As the temperature of the oil is raised by heating from below, minute quantities of guncotton are introduced into the tubes, and the temperature at which it flashes is noted on the thermometer.

## LECTURE XIV.

### NITRIC ETHERS—NITROGLYCERINE.

NITRIC ethers are obtained by the action of nitric acid upon simple alcohols, the reactions being represented by equations similar in every respect to those representing the formation of nitric esters.

As distinguished from nitro-substitution compounds, they possess the general characteristics of nitric derivatives, including the arrangement of the atoms in their molecular structure, as enumerated in previous lectures.

Nitric ethers differ from nitric esters in that, when the latter are treated with reducing agents, the original ingredients are only partially reproduced, the acid being destroyed; whereas by subjecting nitric ethers to the prolonged action of water and dilute alkalies, both the original acid and alcohol are entirely reproduced.

**Nitroglycerine.**—This powerful explosive may be taken as the representative of the class of nitric ethers.

*Discovery and Early History.*—The discovery of the fact that cotton, when immersed in nitric or in a mixture of nitric and sulphuric acids, was converted into a highly explosive substance gave rise to a warm controversy among the chemists of the day as to the nature of the change which had taken place, one party holding that the change was a true chemical one, and was due to the substitution of certain of the components of the nitric acid for certain components of the cotton, resulting in the formation of a new compound



substance; while the other party held that it was physically impossible that so delicate a material as cotton-fibre could change its elements without a more obvious change of structure, and that the change was simply a physical one due to the absorption of the nitric acid in the pores of the cotton, just as nitre is absorbed by paper in the manufacture of touch-paper, and that thus the inflammability of the substance was increased.

It is obvious that with such a difference of views prevailing the true one could only be established by experimental evidence, and hence the promulgation of these views led to many experiments being made upon a large number of substances which were analogous in their chemical characters to cotton. Pelouze, the French chemist, was one of the more active advocates of the theory of exchange, and, among other experiments, he suggested to his pupil Sobrero that he should study the effects of nitric acid on glycerine, because, as the latter was chemically analogous to cotton, it was probable that, if the change was a chemical one, an explosive body would be formed, and it was obvious that if an explosive body was formed it must be due to replacement, for it was exceedingly unlikely that a liquid like glycerine could absorb and retain in its pores, by mere physical force, a liquid like nitric acid.

Sobrero made the experiment and discovered nitroglycerine, which announced its birth by a violent explosion which shattered the windows of the laboratory and wrecked the apparatus.

The great power which this explosive exhibited and the apparent readiness with which it exploded conspired to make chemists somewhat reluctant to pursue the investigation of the character and properties of this substance; and so, although Sobrero made his discovery in 1846, little was done with it until the Crimean War, when it was asserted that Professor Jacobi had manufactured the explosive in quantities for the Russian Government, and that its reputed presence deterred the English from entering the harbor of Cronstadt,

though during this time it was employed in very small quantities as a medicinal agent under the name of *glonoine*.

The practical use of the substance as an explosive agent is due to Alfred Nobel, a Swedish engineer, whose name is indissolubly connected with and pre-eminent in the history of nitroglycerine explosives, and who, about 1860, invented a process for its rapid manufacture, which he patented under the name of *detonating oil*, or *Nobel's Sprengöl*, and between this and 1863 established factories on the continent of Europe for its manufacture on a commercial scale.

At this time Nobel used the same means for exploding the substance as were employed for firing gunpowder, with the addition, sometimes, of a priming-charge of gunpowder; but it was found that, even when confined, the nitroglycerine was but partially exploded. In 1863, however, he discovered that it could not only be exploded with certainty by means of a cap containing mercury fulminate, but that the power developed when thus exploded was enormously greater than could be obtained from it by any other means. The discovery of this fact marks not only an epoch in the history of nitroglycerine, but in that of all explosives, since it revealed to us the method of inducing explosion by detonation.

Great expectations were aroused by the announcement that the enormous force stored up in nitroglycerine was completely under control and could be used at will for doing useful work, and it found its way to the scene of mining operations in many parts of the world.

The introduction of nitroglycerine into the United States was attended with numerous and severe explosions, which for some time discouraged the earlier experimenters in this country.

But it was observed that these accidental explosions were exceptional, and that in repeated instances nitroglycerine had been transported long distances both by sea and by land, and had been stored for considerable periods of time without undergoing explosion; and, as the agent was too valuable a one to be abandoned if its safety could be in any way in-

sured, several chemists were encouraged to further investigate its properties, and to seek to discover and remove the causes which had operated to produce these premature explosions. Notable among these investigators were the American chemists Mowbray and Hill, and through their efforts the difficulties attending the production of a pure and stable substance have been surmounted, so that for many years past nitroglycerine has been manufactured, stored, transported, and used with comparative safety, and with less attendant danger than surrounds gunpowder.

**Chemistry of Nitroglycerine.**—The manufacture of nitroglycerine is based upon the reaction which takes place when glycerine is brought in contact with nitric acid, and which may be represented by



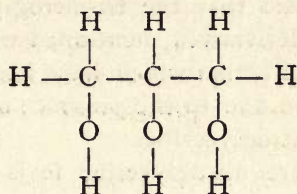
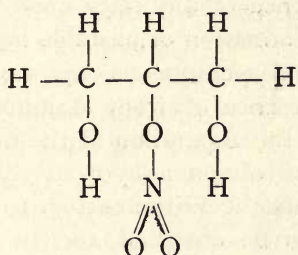
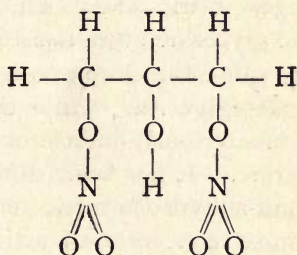
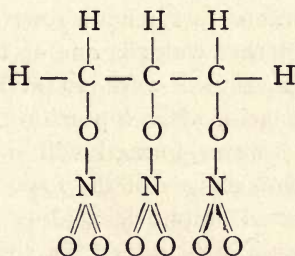
in which one molecule of glycerine being acted upon by three molecules of nitric acid yields one molecule of tri-nitroglycerine (or, better, glyceryl tri-nitrate) and three molecules of water, three atoms of hydrogen in the glycerine being replaced by the three atoms of nitryl ( $\text{NO}_2$ ) in the three molecules of nitric acid.

It is believed to be possible to produce three different nitroglycerines. By replacing one atom of hydrogen in the glycerine by one atom of nitryl the mono-nitroglycerine is formed, having the formula  $\text{C}_3\text{H}_4\text{O}_3(\text{NO}_2)_1\text{H}_1$ . By replacing two of the atoms of hydrogen by two of nitryl the di-nitroglycerine is produced, having the formula  $\text{C}_3\text{H}_3\text{O}_3(\text{NO}_2)_2\text{H}_2$ . By replacing the three atoms we get the tri-nitroglycerine given in the reaction above.

By writing the formula for glycerine as a trihydric alcohol, and as in the case of cellulose, assuming that in the substitution of nitryl for hydrogen in the formation of nitroglycerine only the hydrogen atoms combined as hydroxyl are replaceable, the same reason assigned for the limited degree of nitration in the case of the nitrocelluloses is appli-



cable to the nitroglycerol, and the molecular arrangement may be represented by the following structural formulæ:

Glycerine— $\text{C}_3\text{H}_5(\text{OH})_3$ .Mono-nitroglycerine— $\text{C}_3\text{H}_5\text{O}_3(\text{NO}_2)\text{H}_2$ .Di-nitroglycerine— $\text{C}_3\text{H}_5\text{O}_3(\text{NO}_2)_2\text{H}$ .Tri-nitroglycerine— $\text{C}_3\text{H}_5\text{O}_3(\text{NO}_2)_3$ .

The term *nitroglycerine* is misleading, and has caused many errors to be made upon the assumption that this nitric derivative belongs to the class of nitro-substitution products, instead of being typical of the nitric ethers.

A more correct name for the new explosive would have been *glyceryl tri-nitrate*, or *nitric glyceride*.

The name nitroglycerine has been so generally accepted, however, that it is practically impossible to change it; but it is well to remember that in no way can it be considered as a

nitro-compound, but, for reasons already given, belongs to the class of nitric ethers, a subclass of nitric derivatives.

It is believed also that the tri-nitroglycerine is the only one of the three derivatives mentioned which is stable, and that many of the accidents which have been caused by nitroglycerine have been due to the presence of these other compounds in the tri-nitroglycerine.

To produce pure nitroglycerine it is necessary that we should use the purest anhydrous glycerine and the purest and strongest nitric acid. The presence of any fatty impurities in the glycerine gives rise to the formation of unstable bodies which cause the decomposition and spontaneous explosion of the nitroglycerine, while the presence of iron, alumina, or chlorine seriously interferes with the separation of the nitroglycerine. It has been difficult to obtain anhydrous glycerine and anhydrous nitric acid; hence it is the custom to use the most concentrated articles to be obtained and to mix with them some substance which will absorb the water present and thus render them anhydrous. The importance of using an exsiccating substance is further shown if we refer to the reaction, by the fact that water is one of the products of the reaction, and hence, if we were to start with anhydrous glycerine and nitric acid, after a portion of the glycerine has been converted, the water formed will have so diluted the remainder that there is danger of the lower nitric ethers being formed. Concentrated sulphuric acid is used as the exsiccating substance, and it is added in sufficient quantity to combine not only with the water contained in the original substances, but also with all the water formed during the operation.

But in using the sulphuric acid an element of danger is introduced. The sulphuric acid removes the water by entering into chemical combination with it, a hydrate of sulphuric acid being formed, and this combination is attended with the development of heat. If the temperature is raised much above  $30^{\circ}\text{C}$ . there is danger of the nitroglycerine being exploded, or if an explosion does not result, the glycerine will

be wasted by being converted into oxalic acid and other products which may render the nitroglycerine unstable. Hence it is necessary to keep the mixture cool while the conversion is taking place, and in the process of manufacture this is effected in various ways. Such is the *rationale* of the manufacture of nitroglycerine very concisely stated, and upon it the various processes are based.

*Earlier Laboratory Experiments.*—In his earlier efforts to make nitroglycerine, Sobrero, the discoverer of the explosive, prepared a mixture of sulphuric acid (sp. gr. 1.845) and nitric acid (sp. gr. 1.520) in the proportions of 2 *parts* of the former to *one part* of the latter, and allowed it to cool, and, during the process of nitration, kept the temperature of the mixture below 24° C., by external cooling with ice. Into this mixture he introduced, drop by drop, with constant agitation, *one-half part, by volume, of anhydrous glycerine*. The actual amounts used in these experiments were:

$\text{H}_2\text{SO}_4$  (sp. gr. 1.845) ..... 2.0 oz.

$\text{HNO}_3$  (sp. gr. 1.520) ..... 1.0 “

$\text{C}_3\text{H}_5(\text{OH})_3$  (anhyd. puriss.) ..... 0.5 “

As soon as the conversion was complete, the entire contents of the vessel in which the operation was conducted were poured slowly into a vessel containing 50 parts (oz.) of cold water, whereupon the nitroglycerine, which had formed upon the surface of the acid mixture, settled to the bottom. The supernatant liquid was then decanted, and the nitroglycerine freed from acid by thoroughly washing it with clear water.

In their experiments Praeger and Bertram followed the method pursued by Sobrero without modification so far as the acid mixture was concerned, but used one part of glycerine to eight parts of the mixture, instead of 1 to 6. Liebig, in his investigations, duplicated Sobrero's method.

De Vrij at first tried nitric acid alone, but finally adopted a mixture of nitric and sulphuric acids in varying proportions, also varying the amount of glycerine from one part to six or seven parts of acids.



Kopp prepared his mixture by introducing nitric acid in the form of vapor into the sulphuric acid which had been previously poured into the receivers, and used 8 parts of mixed acids to one part of glycerine. In addition to other innovations in the process of manufacture, Mowbray prepared his acid mixture by introducing sodium nitrate and sulphuric acid into stills and absorbing the nitric acid vapor by sulphuric acid contained in earthenware receivers. For some time he retained the proportions of one part of nitric to two parts of sulphuric acid, and to eight and one-half parts of this mixture he added one part of glycerine.

In passing from the experimental stage to manufacturing nitroglycerine upon a commercial basis, the question of expense became almost as important as the purity of the final product, and in many cases the latter factor has been subordinated to the former, oftentimes at the cost of human life.

**Proportions of the Acid Mixture.**—As in the manufacture of guncotton, so in making nitroglycerine, only the purest and most concentrated acids should be used as well as the purest and most anhydrous glycerine.

The proportions in which the acids are mixed and the proportion of the glycerine to the acid mixture vary with the several processes, and are often regulated as much by the relative cost of material as upon the absolute yield of explosive. The proportions most universally adopted are 3 parts of nitric to 5 parts of sulphuric acid, and to 8 parts of this mixture from 1.0 to 1.15 parts of glycerine are added. The exact proportions in which the acids are mixed to each 100 parts of glycerine are as follows:

	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
Sobrero.....	238	584
Praeger and Bertram.....	266	533
Liebe .....	238	584
De Vrij.....	300	370
Kopp .....	266	533
Mowbray.....	283	567
Champion and Pellet.....	260	520
Modern Dynamite Works .....	270-300	450-500

**Process of Nitration.**—On account of the amount of heat liberated during the reaction by which glycerine is converted into nitroglycerine it is not practicable to introduce all of the glycerine into the acid mixture at once or even to the extent that cotton is immersed in making guncotton.

Also, on account of the viscosity of glycerine which prevents its being intimately and rapidly mixed with the acids, so as to subject every particle to their action, it is necessary to introduce the glycerine very gradually and with constant agitation.

Various mechanical devices have been used for stirring the glycerine so as to thoroughly mix it with the acids, but Dr. Mowbray, of North Adams, Mass., appears to have been the first to suggest the use of compressed air for that purpose, although Prof. Barker had observed about the same time, 1868, that by introducing a current of air into the nitrating mixture not only were the materials more thoroughly mixed, but that the nitrous vapors were partially eliminated and the mixture cooled, thereby rendering possible the production of chemically pure nitroglycerine.

The use of compressed air in mixing the acids as well as in the converter first characterized the Mowbray process of making nitroglycerine.

The same method was used in Europe by Nobel, and was improved by Leidbeck, who, in addition to mixing the glycerine with the acids by means of compressed air, introduced the former into the latter in the form of a shower of spray, with the result that the operation was accelerated and the yield of nitroglycerine increased.

**Manufacture of Nitroglycerine.**—With slight modifications the method of making nitroglycerine commercially may be described as follows:

The plant consists of acid and glycerine tanks, a mixing apparatus or converter, injectors, separators, washing vats, filtering apparatus, storage and discharge tanks, and a denitrication apparatus.

The several parts of apparatus as enumerated are con-

tained in wooden buildings, made as lightly as is consistent with the necessary strength, so that in case of accident the danger from flying débris may be reduced to a minimum.

**Acid Tank.**—In many nitroglycerine factories the acids are purchased already mixed in the proper proportions, being transported in large cast-iron drums (capacity 1500 lbs.) made for the purpose, so that when about “to make a run” the proper amount of mixed acids (which are already cooled) is introduced into the acid tank, which is also of cast iron, and of the capacity required for a single “run” of nitroglycerine. This tank is placed upon a higher level than the converter, into which the acids are introduced by merely opening a faucet. In factories where the acids are made, or where the acids are purchased separately and then mixed so as to insure the proper strength and purity, the acids are first run into a large cast-iron mixing-tank fitted with a stirring-gear (or a compressed-air apparatus), thoroughly mixed, and allowed to cool for twelve or twenty-four hours before being transferred to the acid tank. The use of lead-lined tanks is being gradually discontinued on account of the formation of lead sulphate, which interferes with the separation of the nitroglycerine from the waste acids.

**Glycerine Tank.**—Upon the same level as the acid tank, so that it may flow easily into the converter, is a second cast-iron (or wooden lead-lined) tank of smaller dimensions, into which the necessary amount of glycerine is introduced just previous to starting the process of nitration. The average amount of glycerine used in a “single run” rarely exceeds three hundred and fifty pounds, the amount of acids required for the conversion of this amount of glycerine into nitroglycerine varying according to the table already given. When not forced into the acid mixture in the converter by means of compressed air through injectors, the glycerine is led into the mixing apparatus by a tube perforated with small holes so that it falls upon the surface of the acid mixture in a number of fine streams, the flow being regulated by a tap.

**The Converter.**—This consists of a cast-iron vessel, sur-



rounded by a water-jacket, and contains leaden worms, through which water continually circulates during the process of nitration.

Extending through the centre of the converter is a shaft to which are attached blades so arranged as to form a helical agitator which is kept constantly revolving during the process of conversion. The end of this shaft extends up through the top of the converter, which is also perforated to receive a thermometer and glass tubes through which the nitrous fumes escape. The top is also often fitted with glass plates to enable the operator to watch the reaction going on within the apparatus. At the bottom is a large discharge-tap, by means of which the contents of the converter can be quickly run into the discharge-tanks in case of danger, or into the separators when the nitration is complete.

*Injectors.*—Instead of running the glycerine into the converter by pipes as just described, it is often forced into the acids by means of injectors.

The injectors are so arranged that the glycerine is introduced into the acids from below, and in the form of spray. Two objects are thereby accomplished, namely, the glycerine is finely divided and each particle is immediately subjected to the action of a relatively large quantity of acids, and the cold produced by the expansion of the compressed air serves to reduce the temperature during the reaction, thereby preventing decomposition by local heating, as often occurs when the glycerine is introduced from above, and allowed to drop upon the surface of the acid mixture. There is, however, a corresponding disadvantage attending the use of injectors caused by the reduction of temperature which renders the glycerine viscous and difficult to force through the injectors in very fine spray.

The glycerine should not be introduced into the acids until the temperature of the latter has fallen to about  $15^{\circ}\text{C}.$ , and during the process of nitration the flow of glycerine should be so regulated that the temperature shall not exceed  $30^{\circ}\text{C}.$  Although decomposition does not occur below  $50^{\circ}\text{C}.$ ,

it is possible that this temperature may be attained in certain portions of the mixture due to local heating, and not be registered by the thermometers.

Once this point is reached, it readily extends throughout the mass and is very difficult to regulate; hence the necessity of watching the temperature very carefully during the process of nitration.

Should the temperature rise to  $30^{\circ}$  C., the flow of glycerine should be reduced or entirely shut off, and the agitation increased. If the rise of temperature still increases, and especially if the partially converted charge show signs of extensive "firing," the discharge-faucet at the bottom of the mixing apparatus should be opened and the contents emptied into the discharge-tanks below, all hands leaving the building as rapidly as possible.

The process of nitration may be summed up as follows: The mixed acids are introduced into the converter, water made to circulate through the water-jacket and cooling-worms, the agitator started, and the glycerine-tap opened: The thermometer is now closely watched, as well as the reaction through the glass openings in the top of the converter, and also the color of the fumes escaping through the escape-pipes.

Should the temperature exceed  $30^{\circ}$  C. at any time, or should the reaction become violent, or the escaping fumes indicate "firing," the flow of glycerine should be stopped and the agitation and circulation of the water increased. If in spite of these precautions the "firing" continue to increase, the discharge-tap is opened, and the entire contents of the converter run into the discharge-tank. After the entire charge of glycerine has been introduced into the converter the water is allowed to circulate through the worms for a few moments and the agitation continued to insure thorough nitration before separating the nitroglycerine from the acids.

*First Separator.*—Formerly nitroglycerine was separated from the acids by *skimming* it from the surface by means of wooden scoops. This process was not only tedious and wasteful, but dangerous, and is no longer used. A simple

and safe way of separating the explosive from the acids is to run the contents of the mixing apparatus into a large vessel of water, so that, the acids being diluted and their specific gravity reduced, the nitroglycerine settles to the bottom and the supernatant waste acids may be decanted or siphoned off. This method is expensive, since the acids are entirely lost, and the nitrous fumes produced are extremely disagreeable to the workmen. The method now generally adopted in the large factories is known as the *direct separation*, and depends upon the difference in the specific gravities of the waste acids and the explosive. The specific gravity of nitroglycerine being about 1.60 and that of the waste acids 1.70, the explosive when formed rises to and remains upon the surface of the mixture, so that they can be readily separated.

The *first separator*, in which the great bulk of nitroglycerine is separated from the acids before being washed, consists of a large vessel made of stout sheet lead, having a conical or pyramidal bottom, at the lowest level of which is fitted a separatory funnel connected by gutters or pipes with the discharge-tank or waste-acid tank. The separator is closed with a wooden lead-covered or cast-iron top, through which pass a pipe or flue for conveying away the nitrous fumes, and also a thermometer for registering the temperature of the contents of the apparatus. Through the side of the separator, at the line of separation of the nitroglycerine and waste acids (the same charge being run each time), extends a tap by means of which the explosive can be run directly into the first washing vat as soon as the separation is complete. Since excessive heating is liable to occur in the separator, it is usual to have a stout perforated lead pipe fitted in the lower part of the apparatus, through which in case of necessity compressed air may be forced to agitate the mixture. The greater part of the nitroglycerine separates from the acids very quickly after introduction into the separator, and when anhydrous glycerine and concentrated acids are used, the separation should be complete from one half to three quarters of an hour. When separated, the side-tap is opened and the nitroglycerine is run



directly into the first washing-vat, and the waste acids are drawn off by means of the separatory funnel to the secondary separator, while such nitroglycerine as did not pass through the side-tap also passes through the separatory funnel after the waste acids have been run out into buckets to be added to that already in the washing-vat.

*First Washing-vat.*—The next operation in the manufacture of nitroglycerine is freeing the explosive from acids, the continued presence of which quickly causes decomposition. This is accomplished by continued washing in a large volume of water, constantly changing the wash-water, and from time to time adding sodium carbonate either dry or in the form of solution to neutralize the acid.

The first washing is done in a wooden lead-lined vat, having an inclined bottom, and fitted with two taps, one at the lowest level of the bottom which discharges into a pipe or gutter leading to the second-washing vat, the other slightly above the level of the nitroglycerine in the vat by means of which the wash-water may be run out from time to time so that fresh water may be introduced. The upper tap discharges into a pipe or gutter which carries off the waste water, which in this country is thrown away, but which in Europe is subjected to secondary treatment. Through the bottom of the vat passes a leaden pipe fitted with a "rosette head," by means of which compressed air is introduced so as to agitate the nitroglycerine during the washing. The temperature of the water should be kept at about  $25^{\circ}\text{C}$ ., varying from  $15^{\circ}\text{C}$ . at the beginning of the operation and at no time exceeding  $32^{\circ}\text{C}$ . Instead of adding sodium carbonate, it is better to use a solution of soda, and then only after the wash-water has been changed four or five times, so as to avoid the violent reaction due to the evolution of carbonic acid.

The use of an excess of sodium carbonate is to be avoided so as to prevent the loss of nitroglycerine due to its decomposition by that substance. The washing solution should not contain more than 2.50 per cent of soda.

*Second Washing-vat.*—As it comes from the first wash-

ing-vat, nitroglycerine contains many impurities from which it must be freed. These impurities consist of traces of acids, secondary products of nitration, soda mud, etc. Before filtration the explosive is therefore subjected to a final washing in tepid water contained in wooden lead-lined vats. From the first washing-vat the nitroglycerine is run directly into the second vat, which in this country is generally fitted with a mechanical stirrer or agitator, and thoroughly washed, the wash-water being changed from time to time until the explosive will stand the stability test. The use of hot water, while it accelerates the purification of the explosive by volatilizing the lower nitrogen oxides present, is to be deprecated, since even at  $50^{\circ}\text{C.}$ , under agitation, nitroglycerine is slightly volatile, so that there is an appreciable loss in the yield.

*Filtering Apparatus.*—After the nitroglycerine has been washed and purified so as to be able to stand the standard heat test before being stored, it is further freed from foreign particles and mechanical impurities, which accumulate during the various stages of manufacture and are generally held in suspension by filtration. The apparatus for this purpose consists of a lead-lined wooden vat fitted with an inclined bottom, at the lowest level of which is a tap through which the nitroglycerine may be drawn off. The top of the vat is either wholly or in part movable, and is fitted with the filter proper. The filter consists of a copper or lead cylinder fitted with lugs on the outside of the upper and on the inside of the lower rim. The upper lugs prevent the cylinder from falling through a hole in the top of the vat made to receive it; the lower lugs hold in place a wire-gauze disk which supports the rest of the filter. Upon the wire disk is placed a second disk made of felt, and upon the latter is spread evenly and pressed compactly a layer of common salt to the depth of four or six inches. A second felt disk is placed over the salt and is held in place by a second wire-gauze disk, which is secured by means of lugs on the interior of the cylinder for that purpose.

For the removal of the coarser suspended particles, still

another disk of very fine wire gauze is sometimes placed within the cylinder and about twelve inches above the felt salt-filter. From time to time it is necessary to remove and clean the filter, which may be done by removing the cylinder from the vat, releasing the upper wire-gauze and felt disks, and pouring the salt into water and then removing the lower disks. The salt readily dissolves, and any nitroglycerine held by it is released, settles to the bottom, and may be recovered. The disks are thoroughly washed in warm water, and the filter is ready to be remounted for use, replacing the old salt with a fresh layer. Unless the nitroglycerine is to be used in the manufacture of explosive gelatine or smokeless powder, it is not usual to filter it.

*Storage-tanks.*—Ordinarily nitroglycerine is not stored in a liquid state, the size of the run being limited to the amount required for immediate use in the manufacture of dynamite, so that the explosive is run directly to the mixing-house, to be absorbed by the dope, which converts it practically from a liquid into a solid.

When not immediately used in this way it is stored in lead-lined wooden tanks, or in some case, as in smokeless-powder works, it is dissolved in the proper solvent and stored in copper vessels.

*Discharge-tanks.*—These tanks have been mentioned in connection with the converter, and are used in case of danger resulting from the charge “firing” during nitration. They are lead-lined wooden tanks having a capacity of at least twenty times that of the converter. Formerly they were placed directly beneath the converter, but on account of the nitrous fumes developed whenever a charge is “drowned,” it is better to place them in the open air and connect them with the discharge-pipe of the converter by means of a gutter or pipe. The discharge-tanks are kept constantly half filled with water, which should be changed from time to time, even when unused, so as to prevent the formation of organic matter. These tanks are also fitted with taps at the bottom, so that the water or drowned charge may be drawn off; and



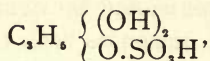
whenever such a charge is run out, care should be taken to collect whatever nitroglycerine may have been formed in the converter before the discharge-tap was opened. The discharge-tanks are also connected by means of pipes with the separators, for the same reason as with the converter.

*Denitrification Apparatus.*—In this country no effort is made (at least at the nitroglycerine works) to save the waste acids.

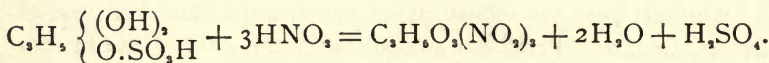
Abroad, however, these acids are treated, and the use of the regained acids reduces considerably the cost of the manufacture of nitroglycerine. The waste acids are introduced into what is called the denitrification apparatus, which consists of a lead cylinder lined with refractory bricks, set with refractory clay and tar. The cylinder is fitted with a false bottom, and is filled with broken quartz. A large earthenware pipe at the top serves to lead the nitrous vapors to a cooling-worm, where they are condensed and collected in large Wolff bottles. Near the top is a funnel by means of which the acids are introduced into the apparatus. The quartz is heated by means of steam, introduced by a pipe which enters the cylinder on a level with the false bottom. A second pipe below this bottom serves to lead the denitrified sulphuric acid into the receiving-tanks.

**Process Employed by the French Government at their Works at Vonges.**—The process of Boutmy and Faucher, which is employed by the French Government at their works at Vonges, differs in principle from any of those described. In this process two mixtures are first prepared: one a mixture of nitric and sulphuric acids in equal proportions, the other a mixture of one part of glycerine to 3.2 parts of sulphuric acid. These are thoroughly cooled, and then mixed together in the proportion of 5.6 parts of the nitric-sulphuric mixture to 4.2 parts of the sulphoglycerine mixture. The whole is placed in an earthen pot, surrounded by water, and the operation is left to take place, which it does quietly, the nitroglycerine separating as formed and rising to the surface of the liquid mass, from which it is eventually skimmed off,

washed, and purified. The theory of this operation is that the glycerine and sulphuric acid form the glycerol-sulphuric acid,



and that this reacts with the nitric acid as follows:



The conversion is conducted in large earthenware crocks, which are placed in troughs filled with cold water. The two mixtures are prepared in the following quantities:

Sulphoglyceric acid	$\left\{ \begin{array}{l} \text{C}_3\text{H}_5(\text{OH})_2 \dots \end{array} \right.$	10 kilogr.	
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \dots \dots \end{array} \right.$	32	“
Nitrosulphuric acid	$\left\{ \begin{array}{l} \text{HNO}_3 \dots \dots \end{array} \right.$	28	“
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \dots \dots \end{array} \right.$	28	“

The forty-two kilogrammes of sulphoglyceric acid are divided into ten equal parts and introduced into ten earthenware crocks, and the nitrosulphuric acid is similarly and gradually run in and the mixture allowed to remain overnight. It is claimed that the heat produced by the Boutmy-Faucher process serves to raise the temperature during conversion to only 22° C., whereas the temperature during the reaction under the ordinary process rises to 41° C.

It is also claimed for this process that it is simple in execution, requires but little apparatus, is safe, and gives a large yield. The claim for safety is questioned on the ground that the nitroglycerine remains for a dangerously long time in contact with the acids, and the explosion at Pembry Burrows in 1883, where this process was used, is cited in support of this criticism. It may be replied that it is now the custom at the factories where the other processes are employed to allow the nitroglycerine and acids to remain in contact for a

long time, until the nitroglycerine separates completely from the acids, so that by skimming the acids may be recovered undiluted, and that the operation is not considered extra hazardous; while, besides, Dr. Dupré found that very impure glycerine and acid had been used at Pembry Burrows at the time of the explosion, and this was sufficient to account for its origin.

In all processes for making nitroglycerine the greatest care must be taken to prevent any accidental mixture of water with the charge in the converter. A very little water shows itself by the greater trouble and slowness in running and in the falling off of the product. If more water enters, the heat will be greater than can be carried away by the usual means of cooling, and the charge is "fired." Usually this means only an active decomposition accompanied by clouds of nitrous vapors.

Slight fires may be stopped by vigorous agitation, but if the firing is persistent the contents of the tub should be run off as rapidly as possible. A constant agitation of the liquid should be kept up during drawing off to prevent separation of the nitroglycerine. When mixing the glycerine in the converter the operation is slowly performed in order to keep the temperature down, but if the temperature is within the limit, the mixing should be performed as rapidly as possible and the nitroglycerine removed from the sphere of action. Rapidity of working is largely dependent upon the quality of acids used, since the heat evolved is least when the strongest acid is used. In general, with highly concentrated acid not only is the product proportionally increased, but the reaction also goes on more uniformly, and is more readily controlled.

**The Yield of Nitroglycerine from the Various Processes.**—From the equation we find that one part of glycerine should yield 2.46 parts of nitroglycerine, but this is never realized in practice. The proportion of nitroglycerine obtained is dependent almost entirely upon the acid. If the glycerine is weak the product will fall off, but the small difference in strength of glycerine ordinarily found exercises



little effect. If the acids are weak, however, the product is markedly less. This does not depend to any extent upon the method or form of apparatus employed, but only upon the acid taken. Weak acids will carry smaller quantities of glycerine and give lower proportional products than strong ones; consequently statements of relative products obtained are of comparatively little value, unless accompanied by a statement of the kind of acid employed and the relative amount of glycerine treated. At Vonges they obtained 1.8, while the Ardeer works get 2 parts, the loss being accounted for by the supposition that other compounds are formed, which are carried away with the acids. In this country we obtain rather more than two parts. By using one part of glycerine to from 7.5 to 8 parts of mixed acids and with care in the preparation of materials 2.2 parts can be obtained.

**Properties of Nitroglycerine.**—At ordinary temperatures nitroglycerine is an oily liquid having a specific gravity of 1.6. Freshly made, by the Mowbray process, it is creamy-white and opaque; but becomes transparent (“clears”) and colorless, or nearly so, on standing for a time, which is dependent on the temperature. When produced by “skimming” it is transparent, but it is often found in commerce to have a yellow or brownish-yellow color.

Although very slightly soluble in it, it does not mix with and is unaffected by cold water. It has a sweet pungent, aromatic taste, and volatilizes in measurable quantities at 50° C.

Nitroglycerine is soluble in methyl, ethyl, and amyl alcohols; in benzene; in carbon disulphide; in all proportions in ether, chloroform, glacial acetic acid, and phenol; and sparingly in glycerine.

The action of various solvents upon nitroglycerine has been carefully investigated by A. H. Elliot, and his results are summarized as follows:

Solvent.	Cold.	Warm.
Water.....	insoluble	slightly soluble
Alcohol: Absolute.....	soluble	soluble
93 per cent.....	"	"
80 " ".....	slowly soluble	"
50 " ".....	insoluble	slightly soluble
Methyl.....	soluble	soluble
Amyl.....	"	"
Ether: Ethylic.....	"	"
Acetic.....	"	"
Chloroform.....	"	"
Acetone.....	"	"
Sulphuric acid (1.845)....	"	"
Nitric " (1.400)....	slowly soluble	"
Hydrochloric acid (1.200).	insoluble—decomposed	slowly soluble
Acetic acid, glacial.....	soluble	soluble
Carbolic acid.....	"	"
Astral oil.....	insoluble	insoluble
Olive ".....	soluble	soluble
Stearine oil.....	"	"
Mineral jelly.....	insoluble	insoluble
Glycerine.....	"	"
Benzene.....	soluble	soluble
Nitro-benzene.....	"	"
Toluene.....	"	"
Carbon bisulphide.....	insoluble	slightly affected
Turpentine.....	"	soluble
Petroleum naphtha (71°-76° B.).....	"	insoluble
Caustic soda, solution 1:10	"	"
Borax, solution 5 per cent.	"	"
Ammonium hydrate (0.980)	"	" ; slightly affected
Ammonium sulph-hydrate.	" ; S separates	decomposed
Iron sulphate, solution ...	slightly affected	affected
" chloride (Fe 1.4 gm. to 10 c.c. H <sub>2</sub> O).....	slowly affected	decomposed
Tin chloride.....	slightly affected,	affected

Nitroglycerine is an active poison, mere contact with it producing nausea, giddiness, faintness, and an especially painful form of headache at the base of the brain. Either in a liquid state or in the form of vapor or fumes, it readily attacks the glands of the moist membranes of the nose or mouth, and is immediately absorbed with the effects mentioned. Persons of highly nervous temperament are particularly sensitive to the action of nitroglycerine, and never become accustomed to it, although the majority of workmen in the factories are quickly inured. Black coffee sometimes affords relief, but the usual antidote administered by phy-

sicians is the acetate of morphia. In many cases the extract of sarsaparilla (Hood's) affords almost instantaneous relief.

Nitroglycerine is rapidly decomposed by alkaline sulphides with the separation of sulphur, and slowly decomposed by an alcoholic solution of potassium hydroxide, by ammonia, alkaline carbonates, hydrogen-sodium phosphate, hot water, ferrous chloride, hydrogen chloride, and sulphuric acid (1:10), though, according to Hay, concentrated sulphuric acid has no action upon it. Its presence may be detected by a solution of aniline in concentrated sulphuric acid which yields a purple color with nitroglycerine, that changes to green on the addition of water.

Freshly made opaque nitroglycerine freezes at from  $-19^{\circ}$  to  $-22^{\circ}$  C., while the transparent or "cleared" nitroglycerine freezes at from  $3^{\circ}$  to  $4^{\circ}$  C., in both cases freezing to a white crystalline mass.

Once frozen it remains in this condition, even when exposed for some time to a temperature sensibly above its freezing-point.

In a frozen state nitroglycerine is less sensitive to concussion than when liquid, and advantage may be taken of this property in order to transport the explosive with comparative safety.

**How to Thaw Nitroglycerine and its Compounds.**—The liability of nitroglycerine to freeze presents difficulties and dangers to those who use it in cold climates, since when frozen it loses a great deal of its force when exploded, and the process of thawing is always attended with danger unless conducted carefully. The best way to thaw nitroglycerine (and nitroglycerine powders) is to place the vessels containing the explosive in a room heated by steam and to so regulate the temperature that it shall not exceed  $50^{\circ}$  C.

For practical use in the field and in mines a special apparatus for thawing nitroglycerine (and its compounds) has been devised, and is generally known as a "*jacketed pot.*" It consists essentially of two water-tight vessels (tin or copper), one considerably smaller than the other, in which the



explosive is placed, and the other to hold water heated to a temperature not exceeding  $50^{\circ}$  C.

The smaller vessel containing the explosive is suspended in the water contained in the larger or outer one and both are covered so as to retain the heat. The water is changed from time to time as it cools until the explosive is thawed. Under no circumstances should vessels containing nitroglycerine be placed in the vicinity of a hot fire, upon heated steam pipes, near steam-boilers, or upon hot bricks, etc., nor should the explosive be placed in the vessel containing the water. Moreover, the outer vessel should be carefully examined before use, in order to be sure that no nitroglycerine has accidentally found its way therein.

The inconvenience presented by frozen nitroglycerine and the danger attending the process of thawing when conducted by ignorant or careless workmen has led to efforts to obviate these difficulties by lowering the freezing-point of the explosive.

In 1885 Nobel discovered that when nitrobenzene was added to nitroglycerine the freezing-point of the explosive was perceptibly reduced. Guttman made a similar observation about the same time, and in his subsequent experiments found that the same result was produced by other benzene and phenol substances, including the pyridine bases and salts.

Practically these discoveries were of little use, since by their addition the freezing-point was very slightly reduced, while the addition of 5 per cent of nitrobenzene sufficed to render it very difficult to explode the mixture, and at the same time it reduced the effect one quarter.

Pure nitroglycerine is not sensitive to friction or moderate percussion, except when pinched between metallic surfaces. If placed upon an anvil and struck with a hammer, only the particle struck, as a rule, explodes, scattering the remainder. A quantity of it has been thrown up by means of a rocket to a height of 1000 feet, from which it fell without being exploded on impact. When, however, in a state of decomposition, it is exceedingly sensitive and explodes violently when

struck, even if unconfined. It must be noted that if completely confined the effect of a blow on pure nitroglycerine may produce explosion, since from its liquid form it is nearly incompressible. In the case cited above local explosion occurs only because the hammer is lifted, and the rest of the explosive is blown away; but if it was so confined that there was no escape for the effect of the explosion of the particle first struck, the whole mass would probably be fired. If nitroglycerine is freely exposed to flame it burns with a brilliant flame and without explosion. If a drop of nitroglycerine be placed on a metal plate and slowly heated up, the nitroglycerine may be completely vaporized without explosion, or if the plate be first heated to incandescence and the drop then placed upon it, the drop will assume the spheroidal condition and eventually volatilize without explosion, but if the hot plate be just below incandescence, so that the nitroglycerine can come in contact with it, the drop explodes with a violent report. The firing-point of nitroglycerine is about  $180^{\circ}$  C. ( $356^{\circ}$  F.), but it begins to decompose under the influence of heat at a somewhat lower temperature.

According to the investigations of Leygue and Champion, nitroglycerine behaves very eccentrically at different temperatures:

At  $185^{\circ}$  C. it boils, evolving nitrous fumes;

$194^{\circ}$  it volatilizes slowly;

$200^{\circ}$  it evaporates rapidly;

$217^{\circ}$  it detonates violently;

$241^{\circ}$  it merely explodes;

$257^{\circ}$  it explodes violently;

$267^{\circ}$  it explodes with less violence than at  $257^{\circ}$ ;

$287^{\circ}$  it explodes as at  $241^{\circ}$ .

By subjecting nitroglycerine to a continuous temperature of  $70^{\circ}$  C. it may be completely evaporated (Hess). Such experiments as those conducted by Leygue and Champion, Hess, Kopp, and others are limited to very minute quantities of the explosive, since to heat larger masses above  $180^{\circ}$  C. is almost invariably followed by an explosion.

**How to Fire Nitroglycerine.**—In order to fire nitroglycerine so as to develop its maximum explosive effect it is necessary to use blasting-caps, or detonators, containing mercury fulminate, it being more sensitive and responding more readily to the initial action of the fulminate than guncotton.

For success, it is also essential that the detonator should be immersed in the liquid so as to be in direct contact with it, but when the caps are fired by means of a running fuse care should be taken that the fuse does not touch the nitroglycerine, as the latter may be set on fire before the cap explodes, and an incomplete explosion, which would produce poisonous fumes and cause a loss of energy, might then result. When fired by a gunpowder fuse only, the action is very uncertain, for sometimes the nitroglycerine is exploded and sometimes not, and even when exploded by this means the force developed is much less than when it is detonated by means of a fulminate. It may be detonated, even when frozen, by means of a heavy charge of fulminate, but the action is not certain. Its insensitiveness when in the frozen condition is shown by the fact that 1600 pounds of the liquid exploded in a magazine which contained also 600 pounds of the frozen, and that the latter was broken up and scattered in every direction without being exploded.

**Decomposition of Nitroglycerine.**—The idea that nitroglycerine, even when pure, spontaneously decomposes at ordinary temperatures after lapse of time is no longer entertained, but on the contrary nitroglycerine has been stored in large quantities for years without any special precaution having been taken to protect it, and without the appearance of any trace of decomposition. Like guncotton, however, nitroglycerine is very susceptible to heat, and even when thoroughly purified it will not stand a temperature of  $100^{\circ}$  C. for a longer period than a few hours without undergoing decomposition. Up to  $45^{\circ}$  C. nitroglycerine properly made and purified remains unchanged almost indefinitely, but beyond that degree of temperature its stability becomes affected within a few weeks.



The action of the direct rays of sunlight is known to cause the decomposition of nitroglycerine as well as the presence of free acid and lower nitric compounds. According to Brull, when, owing to the presence of free acid, decomposition sets in, it proceeds in a slow and tranquil manner, disengaging nitrous vapors, which color the liquid *green*, then developing nitrogen and carbon dioxide and crystals of oxalic acid, until after some months the entire mass is converted into a greenish gelatinous body composed of oxalic acid, water, and ammonia. Sometimes, if the temperature is high, as when heated by the sun, the decomposition is more active, but it by no means always leads to an explosion, though this must depend somewhat upon the quantity involved.

With ordinary care and the most common-sense precautions serious accidents resulting from the decomposition of large quantities of nitroglycerine may be prevented. As just stated, the primary cause of decomposition is the presence of free acid, which may be easily detected by the most ignorant person. Nitroglycerine may be conveniently stored in large earthenware crocks, which should be placed in copper buckets to catch any of the explosive which might by any chance escape from the crocks. When thus stored, the nitroglycerine should be covered with a layer of water, and by testing this water from time to time with litmus paper the least development of acidity in the explosive is made known.

Should the nitroglycerine be stored in tin cans, by removing the caps and suspending the litmus paper immediately over the opening any traces of acidity are at once discovered. In any case, by hanging strips of litmus paper around the interior of the magazine, and examining them from time to time, a very approximate idea of the condition of the nitroglycerine can be formed. Should any slight acidity be developed and the means be at hand, the nitroglycerine should be thoroughly washed as already described. Should the litmus paper show strong acid reaction, and especially if any green color be developed in the explosive, it should be destroyed at

once, the best way of doing this being to explode it in a safe place.

One very frequent source of accidental explosion results from gross carelessness in allowing cans or other vessels in which nitroglycerine has been stored to lie around loosely. In nearly every case particles of the explosive adhere to the vessels, and oftentimes the verdict of "accidental death" should read "deliberate suicide." All such vessels should be destroyed immediately.

**The Use of Nitroglycerine in Blasting.**—In spite of the many accidents that have occurred with it, nitroglycerine has been found to be so valuable that its use has steadily and largely increased. In difficult blasting, where very violent effects are required, it surpasses all others. Its liquid form is a disadvantage, except under favorable circumstances, such as when at the place where it is to be employed. It, however, forms the essential ingredient in a number of solid mixtures, which will be considered later. When used in blasting or similar work it is usually put in tin cans or cartridge-cases. A very good case may be made for it by rolling up stout brown paper into a cylinder of the desired diameter, gluing it, and fastening a cork into one end by choking with fine wire. When dry the case is soaked in melted paraffin. The fuse wires should pass snugly through a cork which fits the open end. This cork may be firmly fixed in the case by means of small tacks. If the bore-holes are water-tight it may be poured directly into them, but it is rarely safe to do this, as there is great danger that some of it will escape through seams in the rock and not be exploded, remaining to cause accident at a future time. Since nitroglycerine is so readily detonated it has the advantage of not requiring strong confinement. Even when freely exposed it will exert violent effects such as breaking masses of rocks or blocks of iron. So in blasting it requires but little tamping. Loose sand or water is entirely sufficient. The relative force of nitroglycerine is not easily estimated, since the effect produced depends greatly on the attendant circumstances. Thus, a

charge of nitroglycerine in wet sand or any soft material will exercise but a slight effect, while the same charge will shatter many tons of the hardest rock. In the former case much more sand would be thrown out by a slower explosion, which would gradually move it, than by the sudden violent shock of the nitroglycerine, which would only compress the material immediately about it. But in the hard rock the sudden explosion is much more effective than the same amount of force more slowly applied.

Nitroglycerine is now but little used in the free state, its principal use in this condition being for "shooting" oil-wells, in order to free them from the paraffins with which they become clogged, or to shake the oil-bearing sandstones so as to increase the yield. The torpedoes used for this purpose consist of tin shells from three to five inches in diameter, and from five to twenty feet in length. These shells are taken to the well empty, the longer ones being in sections which are put together as they are inserted in the well. After the shells are inserted they are filled with the explosive, closed with a tightly-fitting cover to which a strong percussion-cap is attached, and lowered to the bottom of the well (which is often 1500 feet or more in depth) by means of a wire. A perforated iron weight is then strung on the wire, and when the torpedo is in place it is exploded by allowing the iron weight to drop from the surface and strike upon the cap. An advantage which nitroglycerine possesses over gunpowder for use in mining is that in the liquid state it may be poured directly into the bore-hole, and that it may readily and easily be tamped by pouring water upon it, thus avoiding the dangerous process of tamping by ramming, which has given rise to many accidents and caused the loss of many lives. It is obvious, however, that liquid nitroglycerine can be used for this purpose only in holes which tend downwards, while in the operation of mining it is necessary to drive holes in every direction. This, together with the fact already noticed that the liquid state made nitroglycerine a difficult substance to store, transport, and use with safety, impressed the manufacturers



with the necessity for devising some means by which it could be converted into such a solid state that the dangers noted could be avoided, while its great power and susceptibility to detonation could still be used at will. How this has been accomplished will be shown in the next lecture. It should be noted here, however, that a device employed by Nobel to render nitroglycerine insensitive until desired for use was by adding 15 to 20 per cent of methyl alcohol to it. The two liquids were perfectly miscible, and the mixture was completely insensible to blows and even to detonation. When desired for use 6 to 8 volumes of water were added, which precipitated the nitroglycerine out unchanged. It can readily be seen, however, that this scheme was commercially impracticable.

**Tests for Nitroglycerine.**—It is sometimes desirable to ascertain if a substance contains nitroglycerine, without undertaking a complete analysis. Under such circumstances the following simple tests may be applied:

If a liquid is oozing from a substance, or can be squeezed from it, put a drop of it on blotting-paper. If it is nitroglycerine it will make a greasy spot, which will not disappear nor dry away upon standing; struck with a hammer upon iron, it explodes with a sharp report; lighted, it burns with a yellowish to greenish flame, emitting a crackling sound; and placed upon an iron plate and heated from beneath, it explodes sharply.

Again, introduce a few drops into a test-tube, and shake it up with a little methyl alcohol which has been previously tested (by pouring a little of it into distilled water and seeing that it produces no turbidity). After shaking, filter the contents of the tube into a second test-tube, and add a little distilled water to the latter. If the nitroglycerine is present the liquid will become milky, and the nitroglycerine will eventually separate and collect at the bottom of the tube as a heavy lustrous liquid. A much more delicate test is with a solution of aniline and concentrated sulphuric acid as follows:

Aniline ..... 1 volume

$\text{H}_2\text{SO}_4$  (1.84) ..... 40 “

Proceed as in the test just described with methyl alcohol, but before adding the water introduce into the tube a few drops of the aniline solution, which, if nitroglycerine be present, will produce a deep-purple color. The color thus produced changes to green upon the addition of distilled water.

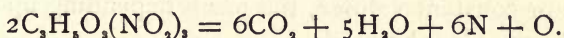
The tests for the condition of nitroglycerine as to stability, etc., do not differ materially from those described for guncotton.

**Test for the Presence of Free Acid.**—Put 2.5 grammes in a thoroughly cleaned and dried test-tube, and add 10–20 c.c. of distilled water. Cork with a clean cork, and shake the tube vigorously for two or three minutes, and allow it to stand for a minute or two. Decant the supernatant liquid into a second tube, which has been previously thoroughly cleaned, and test it with litmus paper, or, better, with methyl-orange.

**Stability or Heat Test for Nitroglycerine.**—Precisely the same apparatus and methods are used as in the case of guncotton, with the following modifications: Five (5) grains of the explosive are used instead of twenty, and the time allowed for the appearance of the color on the test-paper is reduced from fifteen (15) to ten (10) minutes. Great care must be taken in introducing the nitroglycerine into the tube so that the sides of the tube may not be soiled.

**Nitrogen Test.**—In order to determine the exact percentage of nitrogen in nitroglycerine, it is necessary that the sample introduced into the nitrometer shall be perfectly anhydrous. A weighed quantity of the explosive is therefore exposed in a desiccator until constant weight is obtained. The thoroughly dried sample is then introduced into the nitrometer, and the test is performed in the same manner as already described in the case of guncotton. Nitroglycerine having the formula  $\text{C}_3\text{H}_5\text{O}_3(\text{NO}_2)_3$ , the percentage of nitrogen should be 18.50. The ultimate analysis of compounds containing nitroglycerine will be considered subsequently.

**The Explosive Effect of Nitroglycerine.**—From the properties of nitroglycerine as enumerated above, and the numerous methods by which the explosive reaction resulting in the decomposition of the explosive may be provoked, it is evident that the resulting explosive effect may be made to vary between very wide limits. Once started, however, the initiatory step has no influence upon the nature of the products of the reaction, which is generally expressed by the following equation:



According to this equation, we note that nitroglycerine possesses another very exceptional property (not previously mentioned) in that it contains in itself more oxygen than is required for the complete combustion of its elements, the percentage composition of the gaseous products being

CO <sub>2</sub> .....	58.20 per cent
H <sub>2</sub> O .....	19.80 “ “
N .....	18.50 “ “
O .....	3.50 “ “
	<hr/>
	100.00

If we suppose that the substance be converted entirely into gas, it will have a constant volume of 22.32 litres at 0° C. and 76 cm., and a very simple calculation, based upon the above reaction, will show that 227 grammes of nitroglycerine yield 161.82 litres of gas under these conditions.

If, however, instead of aqueous vapor the water be liquid, the volume of permanent gas for a single equivalent of the explosive amounts to 106 litres, or for one kgm. 467 litres.

Berthelot further calculates the heat of total combustion, which in this case is identical with the heat of decomposition as follows: The water being liquid, the heat developed will be

at constant pressure + 356.5 cal.,  
 at constant volume + 358.5 cal.,



The water being gaseous, the heat developed will be

at constant pressure  $+ 331.1$  cal.,

at constant volume  $+ 335.6$  cal.

Or, for one kgm., the water being liquid, the heat developed

will be at constant pressure  $+ 1570$  cal.,

at constant volume  $+ 1579$  cal.

In their investigations Sarrau and Vieille found the heat developed to be  $+ 1600$  cal.

The theoretical temperature may be calculated at constant pressure or constant volume, the result depending upon which of the above values be used.

Thus at constant volume we have

$$t = \frac{335600}{62.24} = 5319^{\circ} \text{ C.}$$

Substituting this value, we find that each equivalent of nitroglycerine produces 3314 litres of permanent gas, which at constant volume exerts a pressure of 23,360 atmospheres.

## LECTURE XV.

### GUNCOTTON BLASTING-POWDERS AND DYNAMITES.

IF we refer to the equation assumed to represent the reaction which occurred when the cellulose nitrate used by Karolyi in his experiments was exploded, or to the formula adopted by Vieille, we see that the products of explosion are those of incomplete combustion. The importance of this fact was quickly appreciated, and almost immediately suggested the practicability of devising an explosive which should be essentially guncotton, but in which the deficiency in oxygen should be supplied by the addition of oxidizing agents so as to obtain more complete combustion.

Several such mixtures have been prepared and have proved successful. In some cases it has been found desirable to produce the explosive in a granular or some regular form, and cementing agents, such as gum, resin, paraffin, etc., have been added for this purpose; but such extraneous matter must be considered in the nature of an adulterant rather than as adding anything to the strength or explosive force of the mixture.

Various nitrates, such as sodium, potassium, ammonium, and barium, have been added to guncotton as oxidizers, with the result that upon explosion all of the poisonous carbonic oxide gas, or at least the greater part of it, is eliminated by being converted into carbonic acid gas. The additional claim, however, that a more powerful explosive results from the admixture of nitrates with guncotton is doubtful.

**Tonite, or Tonite Powder.**—This explosive was introduced into the United States in 1881, and has since that time been manufactured in large quantities under an English patent by the Tonite Powder Company of San Francisco. It consists of a mixture of pulverulent guncotton and barium nitrate, which theoretically should bear the relation of 60.28 parts of the former to 39.72 parts of the latter. Practically, standard tonite consists of

Guncotton.....	52.5 parts.
Barium nitrate.....	47.5 “

The finely divided guncotton and nitrate are thoroughly moistened, and then ground and intimately incorporated under edge rollers until the whole becomes an uniform paste. The paste is then formed into cartridges, which are covered with paraffined paper.

Tonite is whitish in appearance, very dense, burns slowly and without danger; it does not appear to be sensitive to shock or friction, nor does it explode upon the impact of the service bullet. It requires an unusually strong detonator to cause an explosion, the full effect being developed by a special detonator made by the company, known as the “Tonite Cap.” In several experiments, in which ordinary blasting-caps (triple and quintuple force) were used, while no explosion occurred, the cartridge ignited and burned fiercely in the bore-hole until entirely consumed.

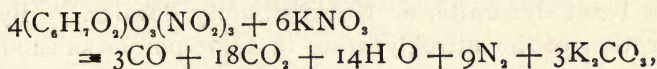
In storage, tonite seems to resist to a remarkable degree the extremes of climate. In strength it stands to the guncotton from which it was made as 82 to 100.

In addition to tonite as described above, and which is now known as *Cotton Powder No. 1*, there have been recently patented two other varieties, called *Cotton Powder No. 2* and *No. 3*, the former consisting of “guncotton thoroughly purified, mixed or impregnated with a nitrate or nitrates and charcoal,” the latter of a “mixture of thoroughly purified meta-di-nitrobenzol and thoroughly purified guncotton, mixed or incorporated with one or more of the following



ingredients, namely, nitrate of potassium, nitrate of sodium, nitrate of barium, and chalk."

**Potentite.**—This is a "nitrated guncotton," identical with tonite, except that potassium nitrate is substituted for the barium salt. If we assume the following reaction to represent what occurs when such a mixture is exploded, viz.:



then the theoretical composition of potentite should be

Guncotton.....	66.20 parts.
Potassium nitrate.....	33.80 "

In practice, however, these proportions are changed somewhat, the amount of guncotton required by theory being reduced about 20 per cent.

The process of manufacture and properties of potentite are almost identical with those of tonite.

**Abel's Guncotton Powder** was patented in 1867, and consists of guncotton mixed with a large proportion of an oxidizing body, such as potassium chlorate or nitrate, or sodium nitrate, or mixtures thereof, with an addition of a small proportion of alkali, or of an alkaline carbonate. The patentee recommended the following proportions:

Guncotton.....	70 to 40 parts.
Oxidizing substances .....	29 to 59 "
Alkaline substances.....	I "

*Bantock's guncotton powder* is essentially the same as that just described, with the addition of a neutral salt.

**Dynamite.**—On account of the many disadvantages attending the handling, storage, and transportation of liquid nitroglycerine, efforts were made soon after the discovery of this explosive, in which it was sought to neutralize these dangers. In 1866 Nobel perfected his invention, and in the following year *dynamite* appeared for the first time in a commercial form. In the English patent the inventor describes his new

production as follows: " This invention relates to the use of nitroglycerine in an altered condition, which renders it far more practical and safe for use. This altered condition of the nitroglycerine is effected by causing it to be absorbed in porous inexplusive substances, such as charcoal, silica, paper, or similar materials, whereby it is converted into a powder, which I call dynamite, or Nobel's Safety Powder." By the absorption of the nitroglycerine in some porous substance it acquires the property of being in a high degree insensible to shocks, and it can also be burned over fire without exploding. It is evident that in thus absorbing the nitroglycerine in a solid material the explosive is not converted into a solid, but is merely retained in the pores of the absorbent through the force of capillarity.

The commercial success attending the invention of Nobel naturally led others to follow where he had led and to examine the suitability of various materials as absorbents, and within an incredibly short period, the market was flooded with dynamite under a great variety of names.

At present dynamite must be considered a generic term under which are included all mixtures of nitroglycerine with substances which absorb and retain it under ordinary conditions of temperature and pressure.

The material used as an absorbent is known technically as the *dope*; and according to the nature of the dope, dynamites may be classified as follows:

- A. DYNAMITE WITH AN INERT BASE, e.g., Kieselguhr Dynamite.
- B. DYNAMITE WITH AN ACTIVE BASE.
  - I. *Combustible Base*, e.g., Carbodynamite.
  - II. *Explosive Base*.
    - a. Explosive Mixture.
      - 1. Mixture of the nitrate class, e.g., Judson Powder.
      - 2. Mixture of the chlorate class, e.g., Vigorite Powder.

*b.* Explosive Compound:

1. Nitro-substitution compound, e.g., Castellanos Powder.
2. Nitric-derivative compound, e.g., Explosive Gelatine.

**Manufacture of Dynamite No. 1.**—The process of manufacture is similar in all dynamites, irrespective of the particular class to which they may belong, and consists essentially of preparing the dope, mixing the purified nitroglycerine with the dope, and making and packing the cartridges, or, when not required in the form of cartridges, storing the explosive in bulk.

Ordinary Kieselguhr dynamite, or dynamite No. 1, consists of a mixture of

Kieselguhr.....	25 parts,
Nitroglycerine.....	75 “

Kieselguhr is a substance which is familiar to all under the names of “tripoli” or “rottenstone,” and possesses in a marked degree high absorptive power. This property, together with the tenacity with which it retained the liquid explosive under considerable changes of temperature; its great chemical stability, and entire inability to react with nitroglycerine; its abundance and consequent cheapness, all combined to recommend it to the inventor.

Kieselguhr is now known to consist of the inorganic remains of countless millions of extremely minute inorganic beings called infusoria or diatoms.

Enormous deposits of this infusorial or diatomaceous silica are to be found near Oberlohe in Hanover, and in this country a large deposit has been traced from Herring’s Bay in Maryland, to a point beyond Petersburg, Virginia; Richmond resting upon a deposit which is 20 feet deep.

When found it is more or less contaminated with impurities, and it has to be calcined to get rid of the organic matter.



The reddish tinge often observed in dynamite is due to a little iron contained in the kieselguhr.

In a pure and dry condition, kieselguhr will absorb three times its weight of nitroglycerine, and will retain it even at the highest ordinary temperature.

Before the guhr can be used for making dynamite, it must be calcined in order to eliminate the moisture and free it from the organic matter it contains.

The calcination is conducted in a reverberatory furnace, the guhr being spread over the bottom of the furnace to a depth of four or five inches, and heated to dull redness. The time of calcination depends upon the quality of the guhr, which from time to time is turned over to insure uniformity. Calcined guhr should not contain more than 0.5 per cent of moisture and organic matter. After being calcined, the guhr is crushed between rollers, passed through fine sieves, dried, and packed away in bags, care being taken to prevent it from absorbing moisture.

Before being mixed with the dope, the nitroglycerine should stand for a day or two to "clear," and should be entirely free from water, since dynamite containing over 0.5 per cent of moisture will *leak*, i.e., the nitroglycerine will exude from the dope.

The nitroglycerine is brought to the mixing-house in buckets made of gutta-percha or lacquered compressed wood-pulp either by hand, train, or trolley line. The mixing is done by hand, the guhr being weighed and placed in lead-lined tanks and the nitroglycerine poured over it. As soon as the ingredients have been thoroughly mixed, the dynamite is rubbed through wire sieves placed over lead-lined troughs, the first sieve being rather coarse (about three meshes per linear inch), and the second finer (about seven meshes per linear inch). In passing through the first sieve the dynamite is more intimately incorporated than where merely kneaded by hand, while the second sieve serves to distribute the nitroglycerine more uniformly throughout the dope. As it comes from the second sieve, dynamite should be neither too wet

nor too dry; in the first case it will leak, and if too dry it will crumble up and can be worked into cartridges only with great difficulty.

From the mixing-house the dynamite is carried to the cartridge-huts in small charges contained in wooden boxes or rubber bags.

By far the greater bulk of dynamite made is used for blasting, and for this purpose it is made into the shape of cylinders for charging bore-holes. The usual sizes of dynamite cartridges (as these cylinders are called), vary from one inch to three fourths of an inch in diameter, and from two to eight inches in length. The cartridges are formed by pressing, the presses being made of gun-metal, and only one press being located in a hut.

Three workmen are assigned to each press, one to work the press, while the other two receive and wrap the cartridges. The press consists essentially of a short cylinder of the diameter of the cartridge to be pressed. Into the cylinder works up and down a piston, the lower end of which is made of *lignum-vitæ* or ivory, and which is actuated by a press-bar. Attached to the upper edge of the cylinder is a canvas bag into which the powdered dynamite is placed by means of wooden scoops, and as the piston descends, the dynamite is forced into and through the cylinder, emerging from the lower end in a compact form, where it is broken off in the length of the required cartridge. Immediately upon leaving the press the cartridges are wrapped carefully to protect them from moisture. Formerly dynamite was wrapped almost exclusively in parchment-paper, and this custom still prevails in Great Britain. On the Continent, however, and in the United States paraffined paper is used.

From the cartridge-huts the cartridges are taken to the packing-houses, where they are packed either for storage or shipment. In Great Britain and on the Continent every five pounds of cartridges are first packed in cardboard boxes which are wrapped generally in water-proof paper. Ten such boxes are packed in a light pine box, the top of which is

secured with screws, or brass or zinc nails. Cardboard boxes are but little used in this country, the cartridges being placed directly in the wooden boxes, which are shellacked on the inside to render them water-proof. In every box of dynamite is placed a printed card of instructions as to the danger of the explosive, together with the precautions to be observed in handling and using it.

With some dynamites sawdust is used to fill the interstices between the cartridges as they are packed in boxes, so that in case of "leakage" during long storage or transportation the nitroglycerine is absorbed. For military purposes dynamite is generally packed in bulk in water-proof metallic cases or bags made of India-rubber.

**Properties of Dynamite.**—Dynamite No. 1 is a granular substance varying in color from a delicate pink to a dirty gray or brown, according to the kind of kieselguhr used as an absorbent. Good dynamite is of the plastic consistency of fresh mould. It should not feel greasy to the touch, nor should there be any trace of free nitroglycerine on the inside of the wrapper of a cartridge. The density of dynamite depends upon the dope, that of dynamite No. 1 being about 1.5. Dynamite possesses the physical properties of nitroglycerine, which is its prime explosive principle, and is equally poisonous. Its firing-point is  $180^{\circ}$  C., and at this temperature it either burns or explodes; if free from all pressure, jar, vibration, or force of any kind, it burns; otherwise it explodes. The sensitiveness of dynamite to blows or shocks increases rapidly with the temperature, so that, according to Eissler, "at  $350^{\circ}$  F. the fall upon it of a dime will explode it." High temperatures below its firing-point cause dynamite "to leak"; hence it should always be carefully tested, and made to resist exudation at the highest temperature to which it may be subjected. When ignited in small quantities in the open air it simply burns fiercely, but when larger amounts are ignited explosion almost invariably results, the explanation being obvious.

Dynamite freezes at about  $4^{\circ}$  C., and when once frozen it



remains in this condition at temperatures considerably exceeding this. Solidly frozen, it cannot be detonated except with great difficulty, and then at a very great loss of its explosive force. Although nitroglycerine is rendered practically safe by freezing it is nevertheless dangerous to cut a frozen dynamite cartridge with a knife, or to ram frozen cartridges in bore-holes. It is therefore customary to thaw the frozen explosive before using it. This operation requires great care, and it is very easily performed, yet the great number of fatal accidents which have resulted either through ignorance or criminal neglect or total disregard of the instructions issued with each package of the explosive as to how to perform the operation, has served in a great measure to prejudice the popular mind against dynamite. In each and every case the accident can be traced to the responsible person or persons, and a few criminal proceedings in this country such as invariably follow such "murders" or suicides" in England would have a very wholesome effect.

These accidents are generally due to the erroneous supposition that because it is reasonably safe to ignite a cartridge of unfrozen dynamite, it is equally safe to warm it upon a shovel, or in a tin can, or in an oven; whereas when heated in this manner the danger limit is approached with each succeeding degree of temperature. *All nitroglycerine preparations, when gradually heated up to their exploding points, become extremely sensitive to the least shock or blow*, and once that point is reached, they no longer simply ignite, but explode with great violence; and further, owing to the poor conductivity of the material, a small portion of dynamite in contact with the source of heat may reach this point and cause the explosion of the rest of the mass, which may be considerably below the danger point.

The necessary precautions to be observed in thawing nitroglycerine and its compounds, and the safest manner in which this operation may be conducted, have already been enumerated and described in a previous lecture. That dynamite is liable to spontaneous decomposition is a very common but

erroneous idea. Equally untrue are the statements that dynamite may be exploded by dropping a cartridge upon the ground, or by the shock caused by slamming a door or window. It is, however, true that dynamite made from impure nitroglycerine decomposes under climatic variations, and especially when subjected to extremely high temperatures, and while in the state of decomposition it is more sensitive to shock than when perfectly stable. For this reason it is often desirable to destroy dynamite which has developed signs of decomposition. The simplest and most effective way to accomplish this object, according to Dr. Dupré, is to place the cartridges or loose dynamite upon the ground in long trains, pour paraffin oil over the mass, and set fire to one end. The combustion will proceed quietly and without danger.

The sensitiveness of dynamite to shock depends largely upon the dope. Generally speaking, dynamite does not explode by blows of wood upon wood, but is liable to do so when struck between stones, and always explodes when the blow is of metal upon metal, except copper and lead.

Dynamite when packed in the form of cartridges or as loose powder will stand very rough handling under ordinary circumstances, since on account of its plastic nature it requires a severe blow to develop sufficient heat to raise the particles struck to the exploding-point. Boxes of dynamite have been dropped in quarries from heights of 150 feet without exploding; and bullets fired from the service rifle will cause explosion upon impact only at distances less than 60 paces. The subject of sympathetic explosion, or the explosion of one mass of dynamite by a second mass fired in the vicinity of, but not in contact with, the first mass, will be considered later.

**Dynamite with an Active Base.**—Very soon after the introduction of dynamite it was discovered that one of the very properties of the new explosive by virtue of which its inventor claimed for it superiority over all other blasting agents, namely, its tremendous power, rendered it wholly unfit for certain kinds of work, such as mining coal, quarrying rock for building purposes, etc. In all such work, as also in

working in soft coal and earth, Dynamite No. 1 was found to be less efficient than black powder. As the energy of the explosive was entirely dependent upon the nitroglycerine contained in it, it was a very simple problem to regulate its force. To reduce this energy and moderate the violence of the explosion it was only necessary to reduce the percentage of nitroglycerine in the dynamite. Experience has proven this to be true, but only up to a certain point, so far as it concerns Dynamite No. 1, since it is claimed that a kieselguhr dynamite containing less than 30 per cent of nitroglycerine cannot be exploded.

In the case of dynamites having active bases, however, the proportion of nitroglycerine may be reduced to less than 5 per cent, and the resulting explosive still be susceptible of explosion. As before stated, dynamites with active bases may be subdivided into two classes, according as the base is a combustible or an explosive. The principle involved in these powders is to substitute for a perfectly inert base an absorbent which will not only retain the nitroglycerine, but, by its own combustion or explosion, either admit of the percentage of nitroglycerine being reduced below the limit possible with ordinary dynamite, thus diminishing the force of the explosive; or, on the other hand, retaining the same amount of nitroglycerine, by the addition of its own force, producing a still more powerful explosive.

**Dynamite with a Combustible Base—Carbodynamite.**  
—As an example of this class, carbodynamite may be mentioned as one of the most recently patented and most favorably received. It consists of 90 parts or less of nitroglycerine and 10 parts of very absorbent charcoal, obtained by carbonizing cork. To every 100 parts of the explosive is added 1.5 parts of sodium or ammonium carbonate. In one variety water is added with the view of rendering the dynamite unflammable. This explosive does not disintegrate or “leak” when exposed to the action of water. It is a black, somewhat friable substance, and compares very well with other dynamites of the same grade.



Another explosive of this class very similar to carbo-dynamite is *Punshon's Explosive*, in which 30 parts of carbonized or charred peat are used to absorb 70 parts of nitroglycerine. In the preparation of the explosive the nitroglycerine "is cleaned by means of chalk mixed with water instead of by the use of alkalies."

**Dynamite with an Explosive Base.**—Dynamites with explosive bases may be classified according as the base is an explosive mixture or an explosive compound, and again, further subdivided according as the base belongs (1) to mixtures of the nitrate or of the chlorate class, or (2) to compounds of the nitro-substitution or nitric derivatives.

**Dynamite with a Nitrate Mixture Base.**—One of the simplest and earliest powders of this class consisted of a mixture of nitroglycerine and mealed gunpowder. In addition to the increased safety of the powder over that of nitroglycerine in a liquid state, it was claimed that the new powder was much more powerful than ordinary dynamite, and that the power actually developed was considerably greater than the sum of the forces of the two ingredients fired separately. In explanation and support of this claim the inventor asserted that when fired the gunpowder was detonated by the nitroglycerine, it being well known that the force developed by gunpowder when detonated is something greater than four times that observed when it is simply exploded. This particular powder was followed by others too numerous to be mentioned.

**Dynamite No. 2.**—This explosive was introduced to compete with powders ordinarily used where great power and local effect was not desired, such as for work in coal-mines, etc. It consists of

Nitroglycerine.....	18 parts
Potassium nitrate.....	71 "
Charcoal.....	10 "
Paraffin.....	1 "

**Dynamite with a Chlorate Mixture Base.**—As an example of dynamites of this class may be mentioned:

**Vigorite**, a powder manufactured by the California Vigorite Powder Company, one grade of which has the following composition:

Nitroglycerine.....	30 parts
Potassium chlorate.....	49 “
Potassium nitrate.....	7 “
Magnesium carbonate.....	5 “
Wood pulp (or fibre).....	9 “

All dynamites of this class possess to a greater or less degree the dangers inherent to all chlorate mixtures.

**Dynamite with a Nitro-substitution Product Base.**—Comparatively few dynamites under this class have attained any practical value; one of the principal ones is known as

**Castellanos Powder**, which consists of a mixture of nitroglycerine, *nitrobenzole*, fibrous material, and guhr. A second variety of this powder having the following composition has been suggested:

Nitroglycerine.....	40 parts
<i>Picrate</i> ... ..	10 “
Sodium nitrate.....	25 “
Carbon.....	10 “
Sulphur.....	5 “
Insoluble salt.....	10 “

The insoluble salt may be a silicate of zinc, magnesium, or calcium, oxalate of calcium, carbonate of zinc, etc.

**Dynamite with a Nitric Derivative Base.**—If we examine the equations supposed to represent the reactions which occur upon the explosion of nitroglycerine and guncotton respectively, it will be seen that when nitroglycerine is detonated free oxygen is evolved, while when guncotton is detonated we have a product of incomplete combustion in the form of carbon monoxide. If, therefore, these two explosives

can be so combined as to use the excess of oxygen in the one to produce complete combustion in the other, we should have theoretically a far more powerful explosive than either of the constituents alone.

**Explosive Gelatine, or Blasting Gelatine.** — In 1875 Mr. Alfred Nobel patented a process by which soluble gun-cotton was dissolved in nitroglycerine by the aid of heat, the result being a tough jelly-like mass which was called *explosive* or *blasting* gelatine. The percentage of nitrocotton in explosive gelatine varies from 4 to 8 per cent. The nitrocotton used should contain not more than 11 per cent of nitrogen, and upon ignition should leave not more than 0.25 per cent of ash. Before mixing with nitroglycerine it is thoroughly dried and very finely comminuted. The nitroglycerine is also very carefully dried beforehand, since the presence of traces of water in the ingredients almost invariably causes the gelatine "to leak." In smaller factories the nitroglycerine is poured into troughs made of sheet copper, which are surrounded by water-jackets through which water heated to about 40° C. is made to circulate. As soon as the nitroglycerine is heated, the time required varying from one-half to one hour, the nitro-cotton is added and stirred in by means of wooden spades until the mass is thoroughly mixed, and then allowed to stand for two hours. At the end of that time it is kneaded by hand until it has a jelly-like consistency, the water is drawn off, and the mass allowed to cool.

In larger factories, special kneading or mixing machines are substituted for the hand process just described.

On account of its toughness, explosive gelatine cannot be made into cartridges as readily as ordinary dynamite, but requires a special machine for that purpose.

A very satisfactory machine for making gelatine cartridges is made upon the principle of an ordinary sausage-making machine, and consists of a conical case containing a concentric shaft and screw blade, the bearings of the shaft being outside of the casing. An opening in the top of the case is fitted with a funnel through which the gelatine is introduced into the



machine, and a second opening at the apex of the cone is fitted with a nozzle (of the diameter of the cartridge), through which the gelatine is forced out in the form of a long cylinder. All of the parts of the machine are made of gun-metal. As the cylinder of gelatine issues from the press, it is cut into lengths by means of a double-bladed knife, the blades being separated at the distance equal to the desired length of the cartridge. The cartridges are then wrapped and packed as already described in the case of dynamite.

**Properties of Explosive Gelatine.**—Explosive gelatine is a translucent elastic substance, varying in color from bright yellow to yellowish brown. It has a specific gravity of 1.6. It does not absorb water, and when placed in it, is affected only superficially, a very small quantity of nitroglycerine being dissolved from the surface, which assumes a whitish color; but no further change occurs, no matter how long the explosive remains immersed.

Unconfined it burns, when ignited, with a bright-yellow flame and a hissing sound, but does not explode. If, however, it is confined and heated to its ignition-point, it explodes violently. Heated slowly it explodes at  $204^{\circ}$  C. ( $399^{\circ}$  F.); heated rapidly it explodes at  $240^{\circ}$  C. ( $464^{\circ}$  F.). At low temperatures it freezes into a hard solid of paler yellow color than when in its normal state, and seems to assume a crystalline structure.

The exact temperature at which it freezes has not been definitely ascertained, as some cartridges have been found to resist freezing when exposed to a freezing mixture for twenty-four hours, while others have frozen readily at  $2^{\circ}$  to  $4^{\circ}$  C. ( $35^{\circ}$  to  $40^{\circ}$  F.). Unlike several dynamites previously considered, explosive gelatine is much more sensitive when frozen than when in the unfrozen state, and can be readily detonated or exploded by the impact of bullets.

When well made, explosive gelatine will not exude nitroglycerine even after repeated freezing and thawing, or when subjected to a temperature of  $90^{\circ}$  F. for 144 hours. Ordinarily gelatine requires very strong detonators in order to

develop its full force, the strength of the detonator varying, however, with the percentage of nitrocotton in the explosive. To insure an explosion of the first order, it is advisable to use at least one gramme of fulminate in firing explosive gelatine. Blasting gelatine seems to be gradually supplanting all other forms of dynamite, both in this country and abroad.

**Military Explosive Gelatine.** — The investigations of Siersch and Roth in connection with those of Trauzl and Colonel Hess have demonstrated that the addition of a small percentage of camphor to ordinary explosive gelatine greatly diminishes its sensitiveness to shock, and especially to the impact of bullets at short range. Such an explosive was introduced in Austria under the name of *military explosive gelatine*, and has the following composition:

Nitroglycerine . . . .	90 parts	} Explosive gelatine . . . .	96 parts
Soluble guncotton. 10	“		
		Camphor . . . . .	4 “

In Italy these proportions are slightly varied, the military gelatine consisting of 92 parts of nitroglycerine, 8 parts of nitrocotton, and 5 parts of camphor.

In appearance the military explosive gelatine resembles ordinary explosive gelatine, but it emits the odor of camphor, and with the exception of the increased insensitiveness, its properties are the same.

Berthelot holds that the effect of the camphor, in increasing the insensitiveness of the explosive, results from the increased elasticity and solidity which the explosive thus acquires, in consequence of which the initial shock of the detonator is propagated through a much greater mass of the substance than it would be if the camphor were not present, so that the sudden and local elevation of the temperature, which is necessary for the chemical and mechanical action which results in detonation, is not realized except by the use of a very powerful detonator. Camphor, according to this theory, does not exert any action on discontinuous powders, and this is shown in practice with potassium chlorate powders.

On account of its solid form and plastic nature, its great power and insensitiveness, explosive gelatine has been regarded as the ideal military explosive, but unfortunately it has in several instances decomposed during storage, and without any apparent cause. One such case of decomposition is recorded by Professor Munroe, of the U. S. Naval Torpedo Station, and others have been noted, although no explosions resulted. At the Artillery School a package containing fifty pounds was subjected to considerable variations of temperature for six years, and on one occasion was immersed in seawater for four days, and when samples were subjected to service tests no signs of decomposition were discovered, while, tested in the pressure-gauge, it showed most conclusively that it had lost none of its explosive force.

Berthelot finds the theoretical pressure of this explosive to be nearly identical with that of nitroglycerine. F. von Rziha finds its theoretical efficiency to be less than that of nitroglycerine in the ratio of 1.40 to 1.45, and, from the discussion of extensive data practically obtained, he supports his conclusion.

General Abbot, however, finds the relative intensity of Dynamite No. 1, nitroglycerine and explosive gelatine, when fired under water to be as 100 : 81 : 117; and with a sample of explosive gelatine furnished by Nobel's Explosive Company of Glasgow he obtained a relative intensity of 142.

In the experiments with the Quinan Pressure-gauge, conducted at the Artillery School, these intensities were as 81.31 : 81.85 : 106.17.

**Gelatine Dynamite.**—Under this name are classed explosives of the explosive gelatine type, whose explosive force has been modified by the admixture of various substances. For general purposes explosive gelatine is too powerful, its use being limited to blasting very tough rock and to military purposes.

As in the case of ordinary dynamite, by making a thinner gelatine and incorporating it with a suitable dope, it is possible to make an explosive which possesses all of the physical



characteristics of explosive gelatine, and the force of which may be regulated according to the nature of the dope. This subclass of explosives is midway between ordinary dynamite and explosive gelatine, and is known as *gelatine dynamite*.

**Forcite** is a gelatine dynamite largely used in the United States, and, on account of its great strength, stability, and cheapness as compared with the cost of explosive gelatine, it has been proposed as a service explosive for charging military submarine mines. The American letters-patent for this explosive describe it as a combination of nitroglycerine with "an inexplusive gelatinizing material and an oxidizing salt." The analysis of one sample of forcite showed its composition to be as follows:

Nitroglycerine.....	98 parts	}	Gelatine.....	50 parts
Nitrocotton.....	2 "			
Sodium nitrate....	76 parts	}	Dope.....	50 "
Sulphur.....	3 "			
Wood-tar.....	20 "			
Wood-pulp.....	1 "			

**Tests for Dynamite.**—Generally speaking, the tests for various dynamites, except in the case of actual analysis, consist in the determination of the quality of the nitroglycerine which forms the active principle of the explosive.

**Separation of the Nitroglycerine from the Base.**—In order to test the nitroglycerine, it is first necessary to separate it from the base, and this is done as follows:

About 25 grammes of the dynamite are placed in a glass funnel which has previously been thoroughly cleaned and plugged with asbestos. The surface is smoothed with a flat-headed glass rod, and kieselguhr, clean and dried, spread over it to the depth of about one eighth of an inch. Water is next added until the layer of kieselguhr is thoroughly moistened, and a clean, dry test-tube is placed under the funnel to catch the nitroglycerine. Water is added from time to time until sufficient nitroglycerine is collected for the several tests. If any water passes through with the nitroglycerine, it is removed

with a piece of blotting-paper, or, if necessary, the nitroglycerine is filtered through a dry filter.

**Test for Free Acid in Dynamite.**—For this test it is not absolutely necessary that the nitroglycerine be separated, but if that has been done, proceed exactly as in the test for ordinary nitroglycerine. Generally it is only necessary to put about one gramme of the explosive in a perfectly clean test-tube, and half fill the tube with distilled water. The tube is then closed with the thumb and shaken vigorously for two or three minutes. As soon as the dynamite settles to the bottom of the tube the water is tested for acidity in the usual way.

**Stability and Nitrogen Tests for Dynamite.**—These tests are conducted in precisely the same manner as has already been described for nitroglycerine, the sample to be tested being taken from the nitroglycerine which has been separated from the base as above indicated.

**Stability Tests for Explosive Gelatine and Gelatine Dynamite.**—In the case of explosive gelatine it is necessary to especially prepare the explosive before subjecting it to the Heat or Stability Test.

About one and one-half grammes of the gelatine are incorporated with twice the quantity of French chalk by working them together gently in a porcelain dish with a wooden spatula.

When intimately mixed, enough of the mixture is introduced carefully into the test-tube, so that when it is gently compressed it will fill the tube to the depth of about  $1\frac{3}{4}$  inches.

The rest of the test is conducted as already described, except that the temperature of the bath is kept at  $160^{\circ}$  F., and the time allowed before discoloration of the test-paper appears is 10 minutes.

**Liquefaction Tests for Explosive Gelatine and Gelatine Dynamite.**—In addition to the usual tests to which all nitroglycerine preparations are subjected, there is an additional test which is applied to explosive gelatine, known as the *liquefaction test*. To make this test, a cylinder is cut from a

gelatine cartridge or stick, the length of which is equal to its diameter, the ends being perfectly flat. The cylinder is then secured to a perfectly flat surface by means of a pin passing vertically through its centre, and exposed to a temperature from 85° to 90° F. for six days and nights (144 hours). During such exposure the cylinder should not diminish more than one fourth of its original length, and the upper cut surface should retain its flatness and the sharpness of its edge.

*The test of liability to exudation* of gelatine requires that there shall be no separation of the general mass of the sample to be tested of a substance of less consistency than the bulk of the remaining portion of the material under any condition of storage, transport, or use, or when the material is subjected three times in succession to alternate freezing and thawing, or when subjected to the liquefaction test hereinbefore described.

In addition to these tests for dynamite, which are readily made and require no particular knowledge of the chemical principles involved, it is sometimes necessary to determine more fully, not only qualitatively, but quantitatively, the character of nitroglycerine preparations.

It is impossible to explain in detail the exact method of procedure in the case of every dynamite. The following outline scheme, however, indicates the general method to be pursued in the analysis of nitroglycerine and nitrocotton powders, and the operator will have little difficulty in applying it to particular cases.





## Outline Scheme for the Analysis of Nitroglycerine Preparations.

I. Exhaust the previously dried substance with anhydrous ether, preferably in a fat-extraction apparatus. (1 and 2.)

1. *Solution*: Divide into two equal parts. (A and B.)

- A.** Allow the ether to evaporate spontaneously, dry the residue in a vacuum of  $H_2SO_4$ , and weigh. Weight represents nitroglycerine, resin, camphor,<sup>1</sup> (sulphur<sup>2</sup>) and paraffin.
- B.** Add phenolphthalein and titrate with alcoholic potash (1 c.c.  $NKHO = 0.330$  resin). Add considerably more  $KHO$ ; evaporate, dissolve the residue in water, shake with ether, and separate.

1. Determine the camphor by difference.

2. As sulphur is very sparingly soluble in ether, it is preferable to extract some of the original substance with water, and treat the residue with alcoholic potash, add bromine, acidify, and precipitate as  $BaSO_4$ .

Ethereal  
Solution.

Aqueous  
Liquid.

Evaporated,  
leaves the  
paraffin.

Add bromine, and acidify with  $HCl$ . Separate<sup>1</sup> the resin, and precipitate with  $BaCl_2$ .<sup>2</sup>  
1. By filtration.  
2.  $BaSO_4 \times 0.1374 = \text{Sulphur}$ .

2. *Residue*: Dry, weigh, and exhaust with water in an extraction-apparatus. (C and D.)

<i>C. Solution :</i>	<i>D. Residue :</i>
Contains metals, nitrates, chlorates, soluble carbonates, etc., the sum of which (except $(\text{NH}_4)_2\text{CO}_3$ ) can be determined by evaporating the solution to dryness at $100^\circ \text{C.}$ , and weighing the residue. The nitrates can be conveniently determined by a nitrometer.	Dry, weigh, and agitate aliquot part with $\text{H}_2\text{SO}_4$ and Hg in a nitrometer. Evolved gas $= \text{N}_2\text{O}_5$ for cellulose nitrates. If any $\text{N}_2\text{O}_4$ is evolved, treat the remaining part of residue with a mixture of 2 parts of ether and 1 part of absolute alcohol. (E and F.)
<i>E. Solution :</i>	<i>F. Residue :</i>
Evaporate and weigh the residue, which consists of mono- and di-nitrocellulose, and collodion guncotton. This may be further examined by the nitrometer.	Dry, weigh, and treat a weighed portion in nitrometer, calculating evolved gas to tri-nitrocellulose. If present, exhaust the remaining part of residue with acetic ether. (G and H.)
<i>G. Solution :</i>	<i>H. Residue :</i>
Contains tri-nitrocellulose.	Weigh, ignite, and weigh again. Loss of weight represents sawdust, cellulose of kieselguhr, charcoal, chalk, and other mineral matter.

**Suggestions on the Analysis of Nitroglycerine Powders.**—The following suggestions will be of value to the beginner in following the outline scheme given above. In order to thoroughly dry the substance so as to determine the percentage of moisture and also prepare it for further manipulation, finely divide and weigh out 10 or 15 grammes and place in a desiccator for 6 or 8 days, and then reweigh. Note loss of weight, replace in desiccator, and reweigh after 4 hours. Repeat this operation until constant weight obtains, and total loss of weight gives the moisture. In the case of ordinary dynamites, it is only necessary to crumble it in the hands, or force it through a sieve before placing it in the desiccator; but gelatine powders must be carefully divided into small pieces by means of a clean platinum or steel spatula.

The dried sample or a portion of it is next transferred to the extractor funnel, the stem of which has been previously plugged with glass, wool, or asbestos fibre, and the funnel and explosive are weighed, and transferred to the extraction apparatus.\*

The selection of a solvent requires careful attention, depending upon the nature of the explosive under examination. Anhydrous ether alone dissolves out the nitroglycerine, leaving the nitrocotton, if present, in the solid residue, whence it is subsequently removed by means of an ether-alcohol solution. A more expeditious method of determining the nitrocotton is to treat the dried weighed sample in a flask with 250 c.c. of ether-alcohol (2 parts of ether to 1 part of alcohol) and allow it to stand for 12 hours. The solution is then filtered, the residue treated with an additional 100 c.c. of ether-alcohol, which at the end of 20 minutes is poured on the filter, and the filtrate added to that obtained from the first treatment. The nitrocotton is next precipitated from the solution by means of chloroform (about 100 c.c. are necessary) and the solution filtered through a linen filter. The precipi-

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\* Any extraction apparatus may be used, but on account of its simplicity and the excellent results obtained with it the Soxhlet apparatus is recommended.



tated nitrocotton is dried on the filter, then detached from it, redissolved in ether-alcohol, again precipitated with chloroform, filtered, dried, detached, dried again to constant weight, and weighed for the percentage of nitrocotton.

When ether alone is used in the extraction apparatus, the solution contains the nitroglycerine, resin, camphor, and paraffin, while the nitrocotton, metallic salts, wood-pulp, etc., remain undissolved.

The manipulation of solution (A) in the scheme may be explained as follows: The dried, weighed residue is treated with solution of sodium hydrate on a water-bath, which dissolves out the resin. From this solution the resin may be precipitated by HCl, collected on a weighed filter, dried, and its weight determined. The paraffin may be separated from the sulphur (after the resin has been removed) by heating the residue with a solution of ammonium sulphide. Upon cooling the paraffin forms upon the surface of the solution as a solid crust, and by puncturing the crust with a glass rod the liquid may be poured off, the paraffin washed with distilled water, dried, and weighed.

The camphor, being readily volatile, may be separated from the sulphur (after the resin and paraffin have been eliminated) by treating the residue with  $CS_2$  and evaporating at a gentle heat until no odor of camphor is detected. The difference in weight will represent the camphor, while the weight of the residue evaporated to dryness will represent the sulphur. The subsequent steps in the scheme require no explanation.

In this lecture no effort has been made to enumerate the infinite list of dynamites which have been proposed for use, but merely to describe the principal properties of a typical powder under each class. For purposes of reference, the names and compositions of a few of the better-known dynamites are given below.

*Giant Powder No. 1.*

Nitroglycerine.....	75.0 parts
Kieselguhr.....	24.5 “
Sodium carbonate.....	0.5 “

*Giant Powder No. 2.*

Nitroglycerine.....	40 parts
Sodium nitrate.....	40 “
Sulphur.....	6 “
Resin (powdered).....	8 “
Kieselguhr.....	8 “

*Dualin.*

Nitroglycerine.....	50 parts
Potassium nitrate.....	20 “
Sawdust.....	30 “

*Atlas A.*

Nitroglycerine.....	75 parts
Sodium nitrate.....	2 “
Magnesium carbonate.....	2 “
Wood-fibre.....	21 “

*Atlas B.*

Nitroglycerine.....	50 parts
Sodium nitrate.....	34 “
Magnesium carbonate.....	2 “
Wood-fibre.....	14 “

*Vulcan Powder.*

Nitroglycerine.....	30.0 parts
Sodium nitrate.....	52.5 “
Charcoal.....	10.5 “
Sulphur.....	7.0 “

*Judson Powder* (R. R. P. grade).

Nitroglycerine .....	5 parts
Sodium nitrate.....	64 “
Sulphur .....	16 “
Cannel coal.....	15 “

*Rendrock.*

Nitroglycerine.....	40 parts
Potassium nitrate.....	40 “
Wood-pulp .....	13 “
Pitch.....	7 “

*Hercules Powder.*

Nitroglycerine.....	40.00 parts
Potassium nitrate.....	31.00 “
Potassium chlorate.....	3.34 “
Magnesium carbonate.....	10.00 “
Sugar.....	15.66 “

*American Safety Powder.*

Nitroglycerine. ....	68.81 parts
Sodium nitrate.....	18.35 “
Wood-pulp.....	12.84 “

*Carbonite.*

Nitroglycerine.....	25.0 parts
Sodium nitrate.....	34.0 “
Sodium carbonate.....	0.5 “
Wood-meal.....	40.5 “

*Stonite.*

Nitroglycerine.....	68.0 parts
Potassium nitrate .....	8.0 “
Kieselguhr.....	20.0 “
Wood-meal.....	4.0 “



*Horsley Powder.*

Nitroglycerine.....	72 parts
Potassium chlorate.....	6 “
Nutgalls.....	1 “
Wood charcoal.....	1 “

*Dynamite de Trauzl.*

Nitroglycerine.....	75 parts
Nitrocotton.....	25 “
Charccal.....	2 “

*Gelignite.*

Nitroglycerine....	96 parts	}	Gelatine.....	65 parts
Nitrocotton.....	4 “			
Sodium nitrate....	75 parts	}	Dope.....	35 “
Sodium carbonate.	1 “			
Wood-pulp.....	24 “			

**Ecrasite.**—The exact composition of this powder is not known, but it is supposed to be a thin blasting gelatine treated with the sulphate or hydrochlorate of ammonium, or both, together with the picrate of ammonium. For a more extensive list of explosives reference may be had to the excellent compilation by Colonel J. P. Cundill, R. A., H. M. Inspector of Explosives.

For further reference the following table giving the percentage of nitroglycerine contained in various grades of some of the dynamites used in this country, together with the trade designations of the several grades, is appended.

ATLAS. (Standard.)		HERCULES.		GIANT.	
Brand.	Per Cent N. G.	Brand.	Per Cent N. G.	Brand.	Per Cent N. G.
E.....	20	No. 4.....	20	Extra.....	20
E+.....	27	No. 4 S.....	27	M.....	20
D.....	30	No. 3 S.....	33	F. F. F. F.....	20
D+.....	33	No. 2.....	40	XXX.....	27
C.....	40	No. 2 S.....	45	No. 2 C.....	33
C+.....	45	No. 2 SS.....	50	No. 2.....	40
B.....	50	No. 1.....	60	No. 2 Extra.....	45
B+.....	60	No. 1XXX.....	75	New No. 1.....	50
A.....	75			No. 1.....	75

ÆTNA.		HECLA.		JUDSON.	
Brand.	Per Cent N. G.	Brand.	Per Cent N. G.	Brand.	Per Cent N. G.
No. 5.....	15	No. 3.....	20	R. R. P.....	5 & under
No. 4.....	20	No. 3X.....	27	F.....	10
No. 4X.....	25	No. 2.....	30	F. F.....	15
No. 3 B.....	27	No. 2X.....	33	F. F. F.....	20
No. 3.....	30	No. 1.....	40	Dbl. Ex.....	27
No. 3 A.....	33	No. 1X.....	50	Trpl. Ex.....	33
No. 3X.....	35	No. 1XX.....	75		
No. 2.....	40				
No. 2X.....	45				
No. 2XX.....	50				
No. 1.....	60				

## LECTURE XVI.

### SMOKELESS POWDERS.

EVER since Von Lenk demonstrated that a perfectly stable product could be obtained by nitrating cotton, efforts have been made to utilize this substance with the view of producing a smokeless explosive to be used as a propellant in firearms. It was very quickly proven that guncotton alone, although almost absolutely smokeless when ignited or exploded, could not be used for this purpose, and it is only comparatively recently that the force of this explosive has been successfully moderated and regulated so as to admit of its use in guns. The more recent investigation and development of smokeless powders dates from the introduction of Vieille's *Poudre B* in 1886 and Nobel's *Ballistite* about the same time; and although all of the so-called smokeless powders may be classified under one or another of the classes of explosives already enumerated, on account of the great importance of this subject it is deemed advisable to consider these new substances separately.

Incidentally it may be stated that the necessity for smokeless powder was created by the development of the full power of magazine small-arms and machine and rapid-fire guns, and although the new industry can be said to have but recently emerged from the experimental stage, still the progress during the past five or six years has been so rapid and satisfactory that it is now the question of but a very short time before the new powders will surely supersede the old black and brown compositions.



Innumerable substances have been used in the various efforts to produce smokeless powders, but at present those powders which seem to promise ultimate success may be broadly divided in two classes, viz.:

(1) Powders consisting essentially of insoluble guncotton or soluble nitrocotton, either alone or mixed in varying proportions, specially treated, or mixed with various other substances with the view of regulating their explosive force.

(2) Powders consisting essentially of insoluble guncotton or soluble nitrocotton, either alone or mixed, to which is added nitroglycerine and such other substances as may be necessary to regulate their force.

Smokeless powders derived from picric acid, the picrates, ammonium nitrate, nitro-derivatives of the aromatic hydrocarbons, have not proven of sufficient value to merit more than passing mention.

**Manufacture of Smokeless Powder.**—The process of manufacture of smokeless powders is similar, whether they belong to the first or second class, and does not differ very greatly from that followed in the case of gelatine dynamite.

The guncotton or nitrocotton is first dried until it contains not more than 0.1 per cent of moisture, and is very finely divided. The presence of a greater amount of water than that specified or small knots of nitrocellulose delays and even prevents at times the full action of the solvent used to effect gelatinization. The substances used as oxidizers, moderators (or *deterrents*, as they are technically termed), neutralizers, etc., are also finely pulverized and mixed, dry or in a paste, or even dissolved in water, or a proportionate part of the solvent to be added after the nitrocellulose is partially or wholly gelatinized. As a measure of precaution, in making powders of the second class the nitroglycerine is also dissolved in a part of the solvent, which serves to diminish very greatly its explosibility. The mixing is effected almost entirely by means of special machines, one of the best being the Werner kneading-machine.

This machine consists essentially of a trough made in two

sections, the upper section being rectangular, while the lower is formed by two half-cylinders placed side by side and so connected that a ridge is formed along the line of junction which divides the lower section into two equal parts.

In each half-cylinder revolves a shaft fitted with helical blades, the clearance between the cylindrical surfaces and the blades and between the blades themselves being very small. The shafts carrying the blades are made to revolve towards each other and at different rates of speed, the number of revolutions of one being about double that of the other, so that the material subjected to this action is constantly changed, and thoroughly kneaded and incorporated.

The machine is generally made of cast iron, and as a matter of precaution is often surrounded with a wrought-iron jacket through which water can be made to circulate. To empty the machine after the incorporation or kneading is complete, the top is removed and the trough tilted so that the paste is thrown out, or when the trough is stationary the shafts and blades are removed, and the paste is taken out by hand.

Before it is placed in the machine the nitrocellulose is partially gelatinized by pouring a portion of the solvent over it, the other substances, thoroughly mixed, are then added to the partially gelatinized nitrocellulose, and the entire mass is put into the machine and the rest of the solvent added.

The machine is then started, and during the process of kneading it is customary to have every one leave the building, although the danger attending the process is very slight. The time required to thoroughly mix the powder varies from about four to eight hours, depending upon the solubility of the nitrocellulose and the amount of solvent used. An excess of solvent causes trouble, due to the difficulty in eliminating it from the resulting paste, and also often causes the paste, when formed into sheets, cylinders, etc., for granulation, to blister and split. Too little solvent, on the other hand, not only delays the incorporation, but is liable to interfere with the perfect homogeneity of the powder.

The treatment of the powder after it comes from the kneading-machines depends upon many things. If the paste contains too large a percentage of the solvent it must be dried before it goes to the press. During this preliminary drying a "skin" forms on the powder, which materially interferes with the subsequent manipulation, so that the question of the proper amount of solvent to be used is very important. Until recently the paste was rolled out into sheets of varying thickness by passing it through steam-heated rollers. These sheets of powder are then placed in a drying-house, where the bulk of the solvent is driven off, and then rolled again to eliminate blisters as well as to perfect the incorporation.

By reducing the distance between the rollers the resulting sheets are made very thin, and should be perfectly transparent and homogeneous. When thicker sheets are required, these thin sheets are folded and passed through rollers set at the required distance. As they come from the rolling-machine the sheets are of the consistency of india-rubber, and pass next to the cutting-machine. With some of the new powders the sheets are "striated" longitudinally to facilitate the subsequent granulation. At present the granulation of smokeless powders is effected by means of circular knives which overlap each other, and which, in the case of powders rolled into sheets, cut the sheets into longitudinal strips, while a horizontal knife rotating at right angles to and against a cutting edge cuts the strips into cubes. The adoption of the cylindrical form of grain, such as is seen in cordite, flite, etc., has necessitated special forms of presses which differ materially from those used in rolling powder-sheets. These machines consist of a large and very strong cylinder, made of cast iron or steel, into which the paste is placed. A piston entering the cylinder through the head, which is securely fastened after the cylinder is charged, is actuated by hydraulic power, and serves first to compress the paste and then to force it out of a die attached to the base of the press. Before passing through the die the paste is generally forced through a plate perfo-



rated with very fine holes so as to prevent clogging. By varying the diameter of the opening or die, the same press may be used for moulding or pressing cylinders, or cords of different sizes. For cylinders of small diameters, such as cordite, filite, etc., the cord or thread is either reeled at once as it emerges from the press on drums, and the drums are then taken to the drying-house, where they remain until all of the solvent is eliminated; or it is received on a canvas belt which passes over steam-pipes, and is discharged into wire baskets, which are subsequently placed in the drying-house, until the thread is ready for granulation. For small arm powder the threads are cut into small cylinders, while in the case of powder intended for guns of large calibre the cylinders are much longer, and even cut into lengths equal to the length of the powder-chamber of the gun. Small-arm powder is dusted and glazed, as has already been described in the case of ordinary gunpowder.

It would be futile to undertake to describe minutely the various processes of manufacture of the many smokeless powders that have been proposed, and the above description is intended only to give a general idea of the manipulation, which is subject to many modifications.

**Properties of Smokeless Powders.**—The requisites for a smokeless powder adapted to military purposes are approximate smokelessness; stability under varying conditions of climate, temperature, and long storage; safety under all kinds of manipulation, such as loading, rough handling in transportation, etc.; freedom from noxious and irrespirable gases when exploded; it should not develop excessive temperatures nor erosive gases which are liable to attack the surface of the bore of the gun; it should give high and regular velocities with uniform and moderate pressures; finally, it should be safe from the possibility of detonation by chemical or mechanical means.

Although several smokeless powders have been invented that give more or less satisfactory results, it may be safely

asserted that no powder yet devised fulfils all of the conditions enumerated above.

The term "smokeless" is relative only, and signifies that the amount of smoke developed on firing is so insignificant as not to obscure either the firer or the object aimed at, and so quickly dissipated as to admit of continuous firing under those conditions.

The question of stability has been fully solved, and there is but little difficulty at present in making a smokeless powder that will stand the stability or heat test not only at the time of manufacture, but after the lapse of several years, and even though the powder be subjected to very considerable climatic and atmospheric changes. The same may be said of the other requisites enumerated, except the question of heat, the regulation of which still causes no little trouble, and, up to the present time, has been moderated only at the expense of other properties which do not admit of the sacrifice.

The color of pure nitrocellulose powders is dull gray or yellow, and when they are pressed into sheets or ribbons they are translucent and very homogeneous in texture. Those made of a mixture of nitrocellulose and nitroglycerine vary in color from a light yellowish brown to a dark opaque brown, while those containing picric acid or the picrates possess the characteristic straw- or golden-yellow color peculiar to those substances. Those powders which are glazed present a metallic gray, black, or reddish appearance, but upon cutting through the grain or washing off the graphite the color peculiar to the composition of the powder is seen. In texture they are smooth and are either of colloidal hardness or tough and of the consistency of india-rubber. As a rule they are insoluble in water and are practically unaffected by it. Smokeless powders are insensitive to the shock of impact or to the passage of a bullet through them. They are more difficult to ignite than black powder, and in order to develop their full force it is necessary to use either a priming of black powder or stronger caps. Although the combustion of the new powders is very nearly complete, and the bore of the gun appears

perfectly clean after the firing of several shots, it is nevertheless necessary to clean the gun carefully after use, since traces of nitrogen compounds remain in the bore, which, combining with the moisture of the atmosphere, will attack the surface. The density of smokeless powders varies with the process of manufacture, while the granulation is governed by the calibre of the gun in which it is to be used, the principal forms of grains being flakes, ribbons, sheets, parallelopipedons, threads, cords, or cylinders, the last either solid, tubular, or multi-perforated.

From the records of trials up to the present time the new powders appear to possess ballistic properties very superior to those of ordinary black or brown powder, much smaller charges being required to produce the same velocities, while the chamber-pressures are much lower, or for equal chamber-pressures the velocities are much higher and uniform.

**Tests for Smokeless Powders.** — The several tests already enumerated and described for the determination of the condition of explosives of the nitroglycerine and guncotton classes are equally applicable to smokeless powders. The time allowed for the stability or heat test will vary slightly according to the composition of the powder, but the exercise of a little judgment will enable the manipulator to decide upon the limit for any particular powder. On account of the great hardness of many of these powders it is necessary to grind them before undertaking a test or analysis. For this purpose any mill with steel conical grinding-surfaces will suffice. The moisture should be determined by drying the ground powder at a temperature not exceeding  $40^{\circ}$  C, which will effectually eliminate all water as well as traces of solvent that may remain, and subsequently exposing the mass in a desiccator.

For a final determination as to the ingredients and the proportions which enter into such a compound, it is only necessary to follow the outline of quantitative analysis for nitroglycerine and guncotton preparations already given with such modifications as may be suggested in any particular case.



**U. S. Naval Smokeless Powder.**—The smokeless powder developed at the U. S. Naval Torpedo Station to be used in guns of all calibres in the U. S. Navy has given very uniform and satisfactory results. It is essentially a nitrocellulose powder, consisting of a mixture of insoluble and soluble nitrocellulose, to which is added the nitrates of barium and potassium and a very small percentage of calcium carbonate. The proportions of these ingredients in the case of powder for the six-inch rapid-fire gun are as follows:

Mixed nitrocellulose (insoluble and soluble)....	80	parts
Barium nitrate .....	15	“
Potassium nitrate.....	4	“
Calcium carbonate.....	1	“

The percentage of nitrogen contained in the insoluble nitrocellulose must be  $13.30 \pm 0.15$ , while that specified for the soluble variety is  $11.60 \pm 0.15$ , and the mean nitration strength of the mixture must show 12.75 per cent of nitrogen. In addition to the special grades of nitrocellulose, as determined by the nitrogen percentages, the purity of the nitrocelluloses is assured by imposing exacting conditions as to their stability, ignition temperature, percentage of unconverted cellulose, and other foreign substances, ash, etc.

The solvent used in making the powder consists of a mixture of

Ethylic ether (sp. gr. 0.720).....	2	parts
Ethylic alcohol (95% absolute by volume).....	1	“

**Process of Manufacture.**—The relative amounts of the insoluble and soluble nitrocellulose having been determined, they are dried separately at a temperature from  $38^{\circ}$  to  $41^{\circ}$  C. until they do not contain more than 0.1% of moisture. The calcium carbonate is also finely pulverized and dried, and is added to the mixed nitrocelluloses after they have been sifted through a 16-mesh sieve. The nitrates are next weighed out and dissolved in hot water, and to this solution

is added the mixture of nitrocelluloses and calcium carbonate with constant stirring until the entire mass becomes a homogeneous paste. This pasty mass is next spread upon trays and redried at a temperature between  $38^{\circ}$  and  $48^{\circ}$  C., and when thoroughly dry it is transferred to the kneading-machine. The ether-alcohol mixture is now added, and the process of kneading begun. It has been found by experiment that the amount of solvent required to secure thorough incorporation is about 500 c.c. to each 500 grammes of dried paste. To prevent loss of solvent due to evaporation, the kneading-machine is made vapor-tight. The mixing or kneading is continued until the resulting grayish-yellow paste is absolutely homogeneous so far as can be detected by the eye, which requires from three to four hours.

The paste is next treated in a preliminary press (known as the "block-press," and is actuated by hydraulic power), where it is pressed into a cylindrical mass of uniform density and of such dimensions as to fit it for the final or powder press.

The cylindrical masses from the block-press are transferred to the final press whence they are forced out of a die under a pressure of about 500 pounds per square inch. As it emerges from the final press the powder is in the form of a ribbon or sheet, the width and thickness of which is determined by the dimensions of the powder-chamber of the gun in which the powder is to be used. On the inner surface of the die are ribs extending in the direction of powder as it emerges from the press, the object of these ribs being to score the sheets or ribbons in the direction of their length, so that the powder will yield uniformly to the pressure of the gases generated in the gun during the combustion of the charge. The ribbon or sheet is next cut into pieces of a width and length corresponding to the chamber of the gun for which it is intended, the general rule being that the thickness of the grain (when perfectly dry) shall be fifteen one-thousandths (0.015) of the calibre of the gun, and the length equal to the length to fit the powder-chamber. Thus, in case of the 6-inch rapid-fire

gun the thickness of the grain (or sheet) is 0.09 of an inch and the length 32 inches. The sheets are next thoroughly dried, first between sheets of porous blotting-paper under moderate pressure and at a temperature between  $15^{\circ}\text{C.}$  and  $21^{\circ}.5\text{C.}$  for three days, then exposed to free circulation of the air at about  $21^{\circ}.5\text{C.}$  for seven days, and finally subjected for a week or longer to a temperature not exceeding  $38^{\circ}\text{C.}$ , until they cease to lose weight.

The sheets, when thoroughly dried, are of a uniform yellowish-gray color and of the characteristic colloidal consistency; they possess a perfectly smooth surface, and are free from internal blisters or cracks. The temperature of ignition of the finished powder should not be below  $172^{\circ}\text{C.}$ , and when subjected to the heat or stability test, it is required to resist exposure to a temperature of  $71^{\circ}\text{C.}$  for thirty minutes without causing discoloration of the test-paper.

**Poudre B.**—Poudre B, or Vieille's powder, was devised for use in the French Lebel rifle, Pattern 1886, and consisted of a mixture of insoluble and soluble nitrocellulose, its exact composition being:

Insoluble nitrocellulose.....	68.21 parts
Soluble nitrocellulose.....	29.79 “
Paraffin .....	2.00 “

The ingredients, to which was added about 20 per cent of water, were worked under light runners until the mixture became perfectly homogeneous, and the paste was then dried between absorbent material until it contained about 5 per cent of water. It was next broken up and sifted through sieves of 0.6 mm. mesh, dried again, and subjected to the action of a mixture of ether-alcohol, and finally rolled into sheets of 0.5 mm. thickness, which were cut into squares, the sides of which were 1.5 mm. in length.

The addition of paraffin serves to diminish its sensibility to shock and to retard its rate of combustion.

Poudre B is claimed to be almost absolutely smokeless. It leaves no residue in the gun except a few unconsumed



grains. It is of the consistency of hard rubber, is honey-yellow in color, and translucent. In the Lebel rifle a charge of 43 grains produced a muzzle velocity of 2050 feet per second with 3350 lbs. pressure per square inch. It loses in power during the first two months after manufacture, necessitating an increase in the charge of about 10 grains in order to produce the ballistic results given, but after that time it remains very uniform, and has proven to be very stable.

**Poudre BN.**—This is supposed to be a modification of Vieille's powder, an analysis of several samples showing its composition to be as follows:

Insoluble nitrocellulose.....	29.13 parts
Soluble nitrocellulose.....	41.31 “
Barium nitrate.....	19.00 “
Potassium nitrate .....	7.97 “
Sodium carbonate .....	2.03 “
Volatiles .....	1.43 “
	<hr/>
	100.87

Poudre BN differs from Vieille's powder in appearance, due to the addition of the metallic salts. It is of a light-gray or drab color, perfectly opaque, and rough to the touch. The thin striated sheets into which it is rolled are brittle, and break readily along the grooves, the distance between which varies according to the calibre of the gun in which the powder is to be used.

For all guns, except small-arms, the strips are broken into proper lengths and packed in canvas bags. For small-arms, the powder is further granulated, the grains being about 1.5 mm. square and about 0.5 mm. thick.

The earlier samples of this powder experimented with by the U. S. Ordnance Department presented no little difficulty in securing proper ignition, a priming of two grains of black powder being required to ignite it and develop its full force. The results of these experiments gave the following ballistic results:

With 45 grains of *BN powder* a mean of six shots (without priming) gave a velocity of 1560 f.-s. and a pressure of 35,000 pounds.

In these trials some little powder remained unconsumed in the shell after firing, so a second series of six shots were fired with a priming of two grains of black powder, with the following result: velocity, 1703 f.-s.; pressure, 52,600 pounds.

A second sample of the same powder, but which was in some respects superior to that just described, was also tested. With this powder ignition was prompt, no priming being required, and the combustion appeared to be complete.

With 40 grains the mean of five shots showed a velocity of 1762.6 f.-s. and a pressure of 46,360 pounds; with 41 grains the mean of ten shots resulted in a velocity of 1857 f.-s. and 53,470 pounds pressure; while with 42 grains the mean of fifteen shots gave the remarkable result of 1904.7 f.-s. velocity and 57,907 pounds pressure.

Notwithstanding the claims as to the excellence of this powder, grave doubts exist as to its stability, and whatever modifications have been made upon the original powder have had but one object in view—to increase its stability under extreme climatic variations.

**Troisdorf Powder.**—This powder, which has been adopted experimentally by Germany as the military service powder, consists of a mixture of gelatinized nitrocellulose and metallic nitrates. It is made in the usual way, rolled into sheets, and granulated. For small arms the thickness of the sheets varies from 0.012 to 0.025 inch, and the grains are square or rectangular, varying between 0.05 and 0.08 inch on a side. The natural color of the powder is light gray, but it is converted into a metallic brown by being coated with graphite. It is almost entirely smokeless, and very free from dust. It does not foul the gun even after extensive firing, evolves no disagreeable or noxious gases, is easily loaded in small-arm shells, has proven very stable, and seems to have given very satisfactory ballistic results.

**Normal Powder.**—This is practically a nitrocellulose compound, manufactured by the Swedish Powder Manufacturing Company, Landskrona, Sweden, and has been adopted as the service powder by the Swiss Army.

Its composition is as follows:

Insoluble nitrocellulose.....	96.21 parts
Soluble nitrocellulose.....	1.80 “
Resin.....	1.99 “

Normal powder is light yellow in color; it is insensitive to shock or friction, very stable, unaffected by moisture, heats the gun comparatively little under rapid firing, and apparently exercises but little injurious action upon the bore of the gun.

**W.-A. Powder.**—This powder is made by the American Smokeless Powder Company, and has been proposed as the service powder for the United States for use in guns of all calibres both in the army and navy. It is made in several grades, according to the ballistic conditions required to be fulfilled, and has given excellent results.

It consists essentially of insoluble guncotton and nitroglycerine, with an admixture of metallic nitrates and an organic substance used as a *deterrent*, or regulator.

The percentage of nitroglycerine varies according to the grade of powder, and may be omitted altogether.

Only insoluble nitrocellulose of the highest grade and thoroughly purified nitroglycerine are used, and the process of manufacture does not differ materially from that described in the case of cordite, except that the nitroglycerine is dissolved in a portion of the acetone, which is the solvent used to affect gelatinization, before it is added to the guncotton. By thus dissolving the nitroglycerine, its explosibility is reduced to a minimum, and the danger attending the subsequent steps in the process of manufacture is very materially diminished.

The powder paste is pressed into solid threads, or tubular cords or cylinders, according to the calibre of the gun in which the powder is to be used. As the threads emerge from the



press they are received upon a canvas belt which passes over steam-heated pipes, and deposited in wire baskets. The larger cords or cylinders are cut into the proper lengths and exposed upon trays in the drying-house, as already described. The powder for small-arms is granulated by cutting the threads into short cylinders, which are subsequently tumbled, dusted, and, if not perfectly dry, again placed upon trays in the drying-house. Before being sent from the factory, in order to secure uniformity, from five to ten lots of 500 pounds each are mixed in a "blending-machine," after which the powder is stored in the magazines until issued.

**Properties of W.-A. Powder.**—The color of the small-arm powder is very light gray, the grains are very uniform in size, dry and hard, and cartridges are easily and uniformly loaded by machine.

The powder for larger guns is of a yellowish color, almost translucent, and is almost as hard as vulcanite. Irrespective of granulation, the powder is almost totally unaffected by atmospheric or climatic conditions, powder submerged for several weeks in a running stream when removed and dried not only showing no signs of instability, but giving practically the same ballistic results as powder just from the magazine. The same may be said of powder exposed to rain, snow, and sun upon the roof of a building for over three months. From these and similar experiments there seems little doubt that this powder is well qualified to stand the conditions of service.

W.-A. powder is not sensitive to the impact of bullets, and when ignited, even in large quantities, unless strongly confined, it does not explode, but burns away. Like all smokeless powders, it exercises a more deleterious action upon the bore of the gun than ordinary gunpowder, and the question of heat is not yet satisfactorily settled. Ballistically it has given excellent results.

**Cordite.**—Cordite is the service smokeless powder adopted by Great Britain for use in small-arms and guns of all calibre. Its composition is as follows:

Nitroglycerine.....	58 parts
Guncotton .....	37 “
Mineral jelly.....	5 “

The conditions to be fulfilled by the nitroglycerine require that, when exposed in a desiccator over calcium chloride for 16 hours it shall not lose more than 0.5 per cent of moisture; that it shall not show more than 0.1 per cent of alkalinity calculated as sodium carbonate; and that it shall stand the heat or stability test for 15 minutes when subjected to a temperature of 80° C. The guncotton is required to contain not more than 0.6 per cent of mineral substances, nor more than about 4 per cent of soluble nitrocotton; and that it shall contain at least 12.50 per cent of nitrogen, as determined by means of the nitrometer test.

**The Manufacture of Cordite.**—The dried guncotton is placed in a brass-lined box or trough and the nitroglycerine poured over it. These two ingredients are thoroughly mixed by hand until the mass present a homogeneous, jelly-like appearance. It is then transferred to the kneading-machine and the solvent—*acetone*—added, and the mass is kneaded for three and one-half hours. The machine is surrounded with a water-jacket, through which cold water circulates so as to regulate the heat and prevent evaporation of the acetone. At the end of three and one-half hours the top of the machine is opened, the mineral jelly (*vaseline*) added, and the kneading is then continued for three and one-half hours longer. From this machine the cordite paste goes into a preliminary press, where it is freed as much as possible from air and formed into a compact mould. The mould is next transferred to the final press, where it is first compressed to the required density and then forced out of the press through dies of varying sizes, depending upon the calibre of the gun for which it is intended. As it emerges from the die, except in the case of the cylinders used in guns of heavy calibre, cordite is reeled upon sheet-metal drums, which are mounted in a reeling-machine similar to those used in reeling yarn.

The filled drums are next taken to the drying-house, in which a temperature of about  $38^{\circ}$  C. is maintained by means of steam-pipes. Depending upon the diameter of the cords or cylinders, it requires from three to eight days to thoroughly dry the powder. In order to secure uniform ballistic results, after the powder is dried it is blended for use in small-arms as follows: The cordite from ten presses which has been wound upon "one-strand" reels is wound upon one "ten-strand" reel, and then the powder on six "ten-strand" reels is transferred to a single drum, forming a rope of sixty strands, which is cut into short lengths forming small cylindrical grains.

Cordite for use in field-guns is cut into lengths of 11 inches, and for guns of heavier calibre into lengths of 14 inches, and placed on trays in the drying-house until perfectly dry.

**Properties of Cordite.**—The color of cordite varies from light to dark brown, depending upon the color of the vaseline used in its manufacture. It has the consistency of hard rubber, and preserves its elasticity even after long storage. It generally retains a smell of acetone. Ignited in the open air it burns fiercely, the cord pencilling at the ignited end. The gases evolved upon explosion are as follows:

CO <sub>2</sub> .....	25.40
CO.....	37.62
N.....	19.55
H.....	17.43
	<hr/>
	100.00

One gramme of cordite yields 877 c.c. of permanent gas and produces 1143 thermal units.

The dimensions of the cords and cylinders used in the various guns are as follows:



Calibre of Gun.	Diameter of Cordite.
0".303.....	0".0375
12-pdr. B. L. {	0 .0500
{	0 .0750
4".7 Q.F. {	0 .1000
{	0 .2000
6".0 Q.F.....	0 .3000
All guns of heavier calibre {	0 .4000
{	0 .5000

The cylinders for heavy guns are tubular. The ballistic properties of cordite are shown in the following table:

Calibre of Gun.	Charge.	Weight of Projectile.	Initial Velocity, Feet per Second.	Pressure, lbs. per sq. in.
0".303	30 grs.	215 grs.	2000 $\pm$ 40	33,000
12-pdr. B.L.	1 lb. 0.5 oz.	12 lbs.	1710 $\pm$ 20	33,000
4".7 Q.F.	5 lbs. 7.0 oz.	25 lbs.	2145 $\pm$ 25	33,000
6".0 Q.F.	14 lbs. 3.0 oz.	100 lbs.	2275	33,500

Cordite has proven to be a very stable powder under very extreme conditions of climate, varying from the extreme arctic cold of Canada to the tropical heat of India, and, like the great majority of these compositions, it has resisted successfully exposure to rain, snow, and all forms of moisture without serious impairment of its ballistic properties.

Up to the present time, however, its effect upon the bore of the gun has proven a serious difficulty. The extreme heat developed by cordite upon explosion, together with the high velocity imparted to the projectile, has served to erode the gun to such an extent as to lead to suggestions of its abandonment as a service powder.

**Ballistite.**—Since its introduction ballistite has undergone considerable modification, not only in the process of manufacture, but in the proportions of the ingredients, which are soluble nitrocellulose and nitroglycerine.

At present ballistite consists of

Soluble nitrocellulose.....	50 parts
Nitroglycerine .....	50 parts

to which is added about one per cent of diphenylamine for the purpose of increasing its stability.

As made at present, the nitrocellulose and nitroglycerine in which the diphenylamine is dissolved are introduced together into a vessel containing hot water and thoroughly mixed with constant stirring by means of compressed air. When mixed as intimately as possible in this way, the paste is freed from the bulk of the water by means of centrifugal machines and pressing between absorbent material, and is then passed between rollers heated by steam to a temperature of from 60° to 90° C. By passing the paste between these rollers repeatedly, the pressure and heat affect a very complete solution of the nitrocellulose in the nitroglycerine, and at the same time eliminate almost entirely all moisture, so that the final sheet is very homogeneous and free from blisters. In color ballistite is very dark, almost black, and has the consistency of rubber. Its average density is 1.6. It is but little affected by moisture, is almost entirely smokeless, but is more susceptible to heat than most of the smokeless powders. As compared with other powders of this class, it has not developed satisfactory ballistic properties.

Although the use of ballistite has been discontinued by Germany, it is still the service powder of Italy, where it is made in large quantities at the royal powder factory at Avigliano. The Italian powder is pressed into fine cords, similar to cordite, and is known as "Filite"; elsewhere ballistite is granulated in the form of cubical grains. Recently ballistite has been coated with graphite so as to prevent the exudation of nitroglycerine, to which it has proven liable, and at the same time to facilitate the loading of small-arm ammunition by preventing the grains from sticking,

**Maxim Powder.**—Excellent results have been obtained from two or three different grades of smokeless powder in-

vented by Mr. Hiram S. Maxim, especially from the experimental powder devised for the 12-inch B. L. rifle.

According to the specifications of his English letters-patent the inventor claims as his object "the production from guncotton of an explosive which will be comparatively smokeless, or will by its combustion produce much less smoke than gunpowder, and which, when used in a fire-arm, will burn slowly as compared with ordinary guncotton, and will exert a high pressure on the projectile.

"The process of manufacture differs somewhat from those previously mentioned, and is described as follows:

"It [tri-nitrocellulose] is first reduced to pulp in water in a rag-engine or pulping or other suitable machine, and then thoroughly washed and dried. The dried pulp is then placed in a strong metal cylinder or chamber, and the air is exhausted from the said cylinder or chamber, that is to say, a vacuum or partial vacuum is created therein. The vaporized solvent, consisting of acetone, either alone or mixed with ether or alcohol, or with both of these substances, is then allowed to enter, or is forced into the said cylinder or chamber.

"The air being entirely removed from the interior of the fibres of the cotton, the vaporized solvent will penetrate to the core of every fibre, and the product will be entirely free from air-bubbles and from empty spaces or interstices such as exist in ordinary guncotton."

After the treatment of the guncotton with the vaporized solvent as above described, which has the effect of perfectly gelatinizing the mass, the paste is either rolled into sheets under considerable pressure between steam-heated rollers, or is pressed through dies into threads, cords, or cylinders—the latter, when intended for guns of large calibre, being multi-perforated.

The flat grains are almost transparent, yellowish in color, and very tough. The cylindrical grains for use in small-arms are whitish and opaque and somewhat brittle, while the powders of larger granulation are almost black, and very hard, resembling very much vulcanite.



The composition\* of the various grades differs between wide limits, all, however, containing nitrocellulose, both insoluble and soluble, nitroglycerine, an alkaline carbonate, and castor-oil.

Analyses by Prof. C. E. Munroe gave the following results:

Flat-grain powder for small-arms—

Insoluble nitrocellulose.....	71.19
Soluble nitrocellulose.....	8.14
Nitroglycerine.....	17.90
Sodium carbonate.....	2.58
Volatiles.....	0.19
Castor-oil.....	Undetermined

Cylindrical grain for small-arms—

Insoluble nitrocellulose.....	46.60
Soluble nitrocellulose.....	6.84
Nitroglycerine.....	44.60
Sodium carbonate.....	1.70
Volatiles.....	0.26
Castor-oil.....	Undetermined

**Wetteren Powder.**—This powder was introduced into the Belgian service in 1889, being manufactured at the royal gunpowder factory at Wetteren. Originally it was a mixture of nitrocellulose and nitroglycerine, which were intimately mixed, amyl acetate being used as the solvent to aid in the incorporation. The original formula has been modified from time to time, and two or more grades of the powder are now made, one at least being essentially a nitrocellulose compound. It is of a dark-brown color and of the consistency of india-rubber. It is rolled into sheets, but its final granula-

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\* In a recent paper Mr. Maxim gives the composition of the later powders, which have proven very satisfactory in the U. S. government tests, as follows:

Guncotton.....	90.00
Nitroglycerine.....	9.00
Urea.....	1.00

tion is very uneven, and the ballistic results have varied between wide limits. It is characterized by the peculiarly pungent odor of amyl acetate (pineapple).

**Leonard Powder.**—This powder, which at one time seemed to promise excellent results, has failed to fulfil the expectations of its inventor. Its composition is as follows:

Nitroglycerine . . . . .	150 parts
Insoluble nitrocellulose . . . . .	50 “
Lycopodium . . . . .	10 “
Urea . . . . .	4 “

**Rifleite.**—This powder is made by the Smokeless Powder Company, at Barwick, Herts, and was proposed for use in the Lee-Metford rifle, 0''.303 cal.

Its composition as shown by analysis is:

Insoluble nitrocellulose . . . . .	74.16 parts
Soluble nitrocellulose . . . . .	22.48 “
Phenyl amidoazobenzene . . . . .	2.52 “
Volatiles . . . . .	0.84 “

Rifleite is a flake powder, the grains being graphited to protect them from moisture. The natural color of the powder is yellowish, due to the organic substance in its composition.

**Indurite.**—Indurite was invented by Professor C. E. Munroe, and is made by “colloidizing” guncotton perfectly free from all soluble nitrocotton, by means of nitrobenzene. One part of guncotton is dissolved in from one to two parts of nitrobenzene, the paste being subsequently run through rollers and granulated or pressed through dies into the form of threads or cords. The powder is then subjected to the action of hot water or steam, which has the effect of hardening or “indurating” it, whence the name *Indurite*.

In addition to the powders mentioned which have been proposed for use in military small-arms and guns of heavy calibre, and which will serve to give an idea of their general

characteristics, manufacture, and properties, there are several others intended almost exclusively for use in sporting rifles and shot-guns. The conditions to be fulfilled by such powders differ greatly from those imposed upon the military explosive, and as a general rule less care is exercised in their preparation.

The composition of some of the better known sporting smokeless powders, as determined by analyses by Professor C. E. Munroe, are given below:

*Schultze Powder.*

Insoluble nitrocellulose.....	32.66
Soluble nitrocellulose.....	27.71
Cellulose.....	1.63
Barium nitrate.....	27.62
Sodium nitrate.....	2.88
Potassium nitrate.....	2.47
Paraffin.....	4.20
Volatiles.....	1.48

*E. C. Powder, No. 1.*

Soluble nitrocellulose.....	53.57
Insoluble nitrocellulose.....	1.86
Cellulose.....	3.12
Barium nitrate.....	34.26
Sodium nitrate.....	3.67
Potassium nitrate.....	1.48
Aurin.....	0.55
Volatiles.....	1.17

*S. K. Powder.*

Insoluble nitrocellulose.....	57.73
Soluble nitrocellulose.....	20.39
Barium nitrate.....	18.08
Potassium nitrate.....	1.24
Aurin.....	1.11
Volatiles.....	1.43



*S. R. Powder.*

Insoluble nitrocellulose.....	46.97
Soluble nitrocellulose.....	28.18
Barium nitrate.....	19.97
Potassium nitrate.....	2.35
Aurin.....	1.06
Volatiles.....	1.45

*American Wood Powder, Grade C.*

Soluble nitrolignum.....	29.25
Insoluble nitrolignum.....	14.06
Lignin (charred).....	28.08
Sodium nitrate.....	15.27
Humus.....	10.32
Volatiles.....	3.01

## LECTURE XVII.

### EXPLOSIVES OF THE SPRENGEL CLASS.

IN 1873 Dr. Hermann Sprengel proposed a new class of explosives which have recently attained great prominence on account of the success that has attended their manufacture and use.

The essential principle of all explosives of the Sprengel class is *the admixture of an oxidizing with a combustible agent at the time of, or just before, being required for use, the constituents of the mixture being themselves separately non-explosive.*

In 1871 Mr. Silas R. Divine filed a caveat in the confidential archives of the U. S. Patent Office to protect his claim to the invention of rack-a-rock, which is a typical explosive of this class, but he published no patent until 1880.

To Dr. Sprengel, therefore, it appears, belongs the credit of the first publication of the general underlying principle of this important class of explosives.

In order to realize and insure a speedy and intimate mixing of the ingredients, Dr. Sprengel's original plan was to use substances one or all of which should be in a liquid state.

Among the oxidizing agents proposed were the various nitrates and chlorates, which are solid, and nitric acid, nitrogen tetroxide, etc., which are liquid; while among the combustible substances were enumerated various nitro substitution products, carbon bisulphide, petroleum, etc. All explosives of this class are powerful, and the majority of them possess a remarkable degree of stability, requiring very

strong detonators to provoke explosion and develop their full force.

On account of the danger attending the mixing of two liquid ingredients when undertaken by ordinary workmen, this subclass of Sprengel explosives was very soon abandoned as a possibility for general use, and can hardly be said to have progressed beyond the experimental stage. The same danger precluded the general use of those explosives made by the admixture of a solid and a liquid; while the third class, namely, the mixture of two solids, presented serious difficulty, although comparatively safe, in that it was found practically impossible to secure uniformity in the resulting explosive without special apparatus with which to mix the ingredients when required for use.

In the hands of practised and intelligent workmen, however, this class of explosives possesses many advantages, especially for military purposes.

**Rack-a-Rock.**—This is one of the best known of these mixtures, and consists of potassium chlorate and mono-nitrobenzene (sp. gr. 1.33). According to General Abbot, the best results are obtained when these ingredients are mixed in the following proportions:

Potassium chlorate.....	79 parts
Mono-nitrobenzene.....	21 “

The ingredients are transported and stored separately until required for use. Two general methods of mixing are pursued, one by dipping the chlorate cartridges in a pail of the liquid, the other by placing the cartridges in a pan arranged with cells to receive them, and pouring the liquid over them.

In the first case, the cartridges are placed in tiers in a wire basket made for the purpose, and the basket lowered into the pail containing the liquid, subjecting the cartridges to immersion from 3 to 6 seconds, depending upon their size. The basket is then withdrawn, the cartridges allowed to drain



for a few moments, and at the end of ten minutes they are ready for use.

The mixing is accomplished more nearly according to the required proportions by means of the saturation process than by dipping as just described.

Each size of cartridge has its corresponding cell and cup, into which it is placed; and on each cartridge is poured exactly one full cup of the liquid. As soon as the liquid is entirely absorbed, the cartridge is removed, and after the lapse of ten minutes, as before, it is ready for use.

Rack-a-rock is a compact solid having a specific gravity of 1.7. According to General Abbot, "it decrepitates with difficulty when hammered on an anvil, but hardly ignites on wood." A fuse containing 24 grains of fulminating mercury fails to explode a cartridge unconfined or loosely confined. A cartridge struck by a bullet from a Springfield rifle flashes, but does not detonate. Ordinary friction seems to have little tendency to cause explosion. These facts show it to be quite safe to handle, even when ready for use, and it has given excellent results in rock-blasting under General Newton at Flood Rock, 240,399 pounds being used on that occasion.

When tested within fifteen minutes after mixing, samples of this explosive have been found quite sensitive to friction between metal surfaces, and even when gently rubbed in a porcelain mortar; while its sensitiveness to percussion has been found to be equal to that of Dynamite No. 1.

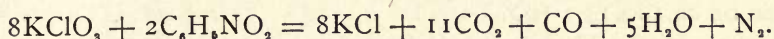
It is very generally believed that the fullest effect to be derived from an explosive demands perfect explosion, which in the case of rack-a-rock would require that all the carbon present should be oxidized to carbonic acid, the hydrogen to water, and the nitrogen set free. Under this supposition, therefore, the following equation would represent the explosion of rack-a-rock:



Whence we see that theoretically the proportions of the ingredients should be:

Potassium chlorate.....	89.9 parts
Mono-nitrobenzene.. ..	19.1 “

Accepting, however, the proportions given by General Abbot, the equation to be assumed to represent the explosion of rack-a-rock, when the maximum effect is developed, is



Examining this equation, we see that instead of all of the carbon being oxidized to carbonic acid, a small percentage appears in the form of carbonic oxide. And what appears to be true in the case of this explosive has been found to obtain in many others.

**Hellhoffite.**—In 1885 Hellhoff and Gruson patented a new variety of this class of explosives, which is now known to consist of meta-di-nitrobenzene and nitric acid. By dissolving the di-nitrobenzene in concentrated nitric acid until a thoroughly saturated solution is obtained the new explosive, known as hellhoffite, appears as a dark red or brown liquid.

Approximately the proportions are as follows:

Meta-di-nitrobenzene.....	47 parts
Nitric acid (sp. gr. 1.50).....	53 “

Thus made hellhoffite does not appear to be a new product, but merely a solution, and, if by any chance the mixture is not required for immediate use, by adding water gradually to the acid it may be diluted to such an extent that the di-nitrobenzene will be no longer held in solution, and will recrystallize. By straining the mixture the crystals can be separated and dried, and are then ready to be used again. Of course the diluted acid cannot again be used for making the explosive. To develop the full force of this explosive requires the use of a detonator twice as powerful as that used to explode ordinary dynamite.

Extensive experiments were carried out to prove the superiority of hellhoffite over all other existing explosives

both for industrial purposes and for military use wherever a perfectly safe but violent explosive was required. Briefly stated, the special advantages of this explosive are:

1. When detonated by the fulminate of mercury, it is more powerful than nitroglycerine. Experiments in this laboratory show the relative intensities of the two explosives to be as 106.17 : 100.

2. It may be stored and transported with perfect safety as regards concussion, since it cannot be exploded by a blow, shock, or an open flame.

On the other hand, however, it possesses certain disadvantages:

1. It is a liquid.

2. The acid contained in it is so volatile that it can be stored only in perfectly closed vessels.

3. It is rendered completely inexplusive by being mixed with water, and therefore cannot be employed for submarine work.

4. On account of the action of the acid on the copper cases of the detonators the latter require particular treatment and inspection before use.

The results of the experiments with this explosive conducted by the German government have not been made known.

**Oxonite.**—Like hellhoffite, which it very closely resembles in appearance, this explosive is a simple solution, and is made by dissolving picric acid in concentrated nitric acid.

The action is perfectly quiet and is attended with a slight fall of temperature of the solution.

In experiments in this laboratory it was found that the proportions required to produce a perfectly saturated solution were as follows:

Picric acid . . . . .	54 parts
Nitric acid (sp. gr. 1.50) . . . . .	46 “

• These proportions, however, are subject to slight changes, depending upon the strength of the nitric acid, and also upon



the condition of the other ingredient, whether merely pulverized before being added, or *fused* and pulverized. This last condition was also found to materially affect the strength of the resulting explosive. For instance, assuming the standard nitroglycerine to have a value of 100, the relative intensities of the oxonite made with picric acid *not fused* and *fused* were as 64.24 : 69.51.

Oxonite is much less powerful than hellhoffite, and requires a very powerful detonator to develop its full force; it is unaffected by blows or shock, and is entirely insensitive to friction.

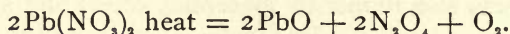
It is generally conceded that this explosive is identical with the "A-explosive" which was surrounded with such profound mystery until the occurrence of serious accidents during its trial as a bursting charge for shells proved it unfit for service. Other accidents, notably one in 1884, have caused oxonite to be regarded with suspicion; but in the case of every accident the cause can be traced to the disregard of the precaution against allowing the nitric acid to gain access to the contents of the detonator. When prepared commercially, the picric acid, sometimes with the addition of a nitrate, is packed in a muslin bag, which also contains the nitric acid in a hermetically sealed glass tube. This tube is broken by a blow before the cartridge is required for use.

**Panclastite.**—This substance is made by mixing liquid nitrogen tetroxide ( $N_2O_4$ ) with combustible substances, such as the hydrocarbons, vegetable, animal, and mineral oils, fats and their derivatives, but preferably with carbon disulphide. The inventor, Mr. Eugene Turpin, proposes that the two ingredients should be kept apart until required for use, when they may be mixed in varying proportions, depending upon the particular work to be accomplished. The proportions which yield the most sensitive mixture are approximately

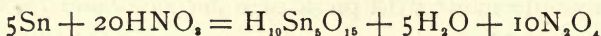
Nitrogen tetroxide.....	3	volumes
Carbon disulphide.....	2	"

The nitrogen tetroxide may be prepared:

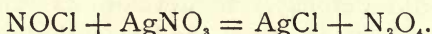
1. By heating lead nitrate:



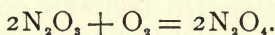
2. By acting on tin with nitric acid;



3. By acting on nitrosyl chloride with silver nitrate;



4. By the union of oxygen with nitrogen trioxide;



When nitrogen tetroxide is made by any of these processes and passed through a freezing-mixture, it condenses into transparent crystals, which melt at  $-9^\circ$ , and which when once melted do not resolidify until cooled to  $-30^\circ$ . Above  $-9^\circ$  it forms a mobile liquid, having a specific gravity of 1.451, which boils at  $22^\circ$ .

The vapors from this gas are of reddish color; possess a pungent, suffocating odor and an acid taste; they stain the skin bright yellow, and are irrespirable.

In making the explosive the temperature falls about  $20^\circ$ .

*Panclastite* ignited in the open air burns with an exceedingly brilliant flame; confined in a vessel and ignited, it burns until the pressure of the gases produces an explosion. Exploded, however, by a fulminate, whether in the open air or confined, the explosion is complete and powerful, whereas in the former case only a portion of the substance explodes, the remainder burning away quietly.

The usual advantages are claimed for this explosive, namely, greater power than dynamite, perfect safety of the constituents separately, so that they may be stored and transported without danger of fire or explosion, and insensitiveness of the mixture to blows or friction.

**Romite or Romit.** — This explosive was invented by M. Sjöberg, a Swedish engineer, and consists of

Ammonium nitrate . . . . .	100 parts
Nitronaphthaline . . . . .	1 “
Paraffin oil . . . . .	2 “
Potassium chlorate . . . . .	7 “

The first three ingredients are intimately mixed, and when required for use the potassium salt is incorporated.

The earlier experiments with romite, especially tests looking towards its adoption as a shell-charge by the Swedish artillery, seemed to promise success, but an investigation into the cause of some thirteen explosions which occurred in various places in Stockholm during a heated period of 1888 disclosed the fact that in eleven of the thirteen places *romite* had been stored, and the accidents were *all* attributed to the “spontaneous ignition” of this explosive. Since that time little or no attention has been devoted to the further development of this explosive.

**Practical Value of Sprengel Explosives.**—Although the great power of this class of explosives is undoubted, still their value as practical explosives for general use is greatly diminished by the fact that the proper incorporation of the several ingredients (or even of two) requires a higher degree of intelligence than is ordinarily found among the practical miners. Moreover, with those explosives of this class into which nitric acid or carbon bisulphide enters as one of the principal ingredients the incorporation in confined spaces, such as mine-galleries, etc., is open to serious objection.

Finally, with such explosives as hellhoffite and oxonite, which contain a large percentage of concentrated nitric acid, it is necessary to protect the detonator from the action of the acid by thoroughly coating it with paraffin or in some other efficacious manner. Should the copper capsule containing the detonating mixture come into contact with the acid, it would be quickly corroded and a premature explosion would almost surely result.

On the other hand, the practical advantages of explosives of this class for military purposes are apparent. Safe in



storage and transportation, the only source of danger seems to lie in proper manipulation when the explosive is required for use, and this, under the supervision of intelligent officers, can be reduced to a minimum. Control over the power of the explosive lies within the hands of the manipulator, so that by varying the proportions of the ingredients an explosive varying in force from that of dynamite to that of ordinary blasting-powder can be prepared at will.

## LECTURE XVIII.

### FULMINATES, AMIDES, AND SIMILAR COMPOUNDS.

**Chemical Constitution of the Fulminates.**—The fulminates are now regarded as metallic salts of a hypothetical fulminic acid, or fulminate of hydrogen, the formula for which is  $\text{H}_2\text{C}_2\text{N}_2\text{O}_2$ .

This acid, which has an intermediate composition between cyanic acid,  $\text{HCNO}$ , and cyanuric acid,  $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ , has never been obtained in a separate form, but the fact of the existence of double fulminates and acid fulminates; and the intimate relation existing between the fulminates and the cyanogen compounds, are accepted as evidence of the existence of such a compound.

Although the constitution of the fulminates is but little understood, they are generally considered iso-nitroso-compounds, the principal salt being that derived from mercury.

**Mercury Fulminate.**—In the Philosophical Transactions for the year 1800 Howard stated that when mercury was heated with nitric acid and alcohol an explosive compound was formed. This substance, which was subsequently known as Howard's fulminating mercury, appeared as a whitish salt which crystallized in acicular needles possessing a saline taste, and which when dried explode with extreme violence when struck upon metal, or when a drop of sulphuric acid was poured upon it. In the earlier attempts to substitute mercury fulminate for gunpowder as a propelling agent, it was found to impart but low velocities to the bullets, while in nearly

every case it burst the gun. In other words, the extreme violence of its action locally, and the great difficulty met with in controlling this action, led to its disuse, until the introduction of percussion-caps and primers.

Quite a number of methods have been proposed and used for the manufacture of mercury fulminate, but the following has given the most satisfactory results when small quantities are required for experimental purposes.

Introduce into a flask, of about 300 c.c. capacity,

Mercury.....	10 parts
Nitric acid (sp. gr. 1.40).....	120 "

and heat gently until all the mercury is dissolved, and allow the solution to cool, shaking the flask from time to time to secure homogeneity, and then pour it into a flask (2000 c.c. capacity) containing

Alcohol (95 per cent).....	110 parts
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The latter flask should be placed in the open air or under a hood, so that the fumes evolved during the reaction may be rapidly dissipated, and also at a distance from any naked light, or other source of ignition.

As soon as the reaction is finished, fill the flask half full of filtered water and allow the grayish powder to settle. The supernatant liquid is then poured off, and the washing is repeated as long as the decanted wash-water shows any traces of acid reaction. At an atmospheric temperature of 15°.5 C., or above, no heating is required to start the reaction; but should the temperature fall below 60° (shown by the reaction ceasing), the flask should be placed in a vessel containing warm water until effervescence recommences. During the washing *extreme care* must be taken that no fulminate accumulates on dishes, beakers, or floors, or is carried into drains, for serious accidents have resulted from minute quantities having been spilled and having remained unnoticed until dry, when an explosion resulted. Should any be spilled, it



should be destroyed at once by means of a solution of an alkaline sulphide.

The reactions attending the formations of mercury fulminate by this process may be represented as follows:

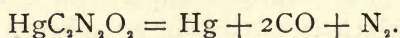
1.  $3\text{HNO}_3 + \text{Hg} = \text{Hg}(\text{NO}_3)_2 + \text{HNO}_2 + \text{H}_2\text{O}.$
2.  $\text{C}_2\text{H}_5.\text{OH} + \text{HNO}_2 = \text{C}_2\text{H}_5.\text{NO}_2 + \text{H}_2\text{O}.$
3.  $\text{C}_2\text{H}_5.\text{NO}_2 + \text{HNO}_2 = \text{H}_2\text{C}_2\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}.$
4.  $\text{H}_2\text{C}_2\text{N}_2\text{O}_2 + \text{Hg}(\text{NO}_3)_2 = \text{HgC}_2\text{N}_2\text{O}_2 + 2\text{HNO}_3.$

**Manufacture of Mercury Fulminate.**—Several methods for making mercury fulminate upon a commercial scale have been devised, notably those of Howard, Liebig, and Chevalier, all of which possess greater or less merit. At present, however, the process of Chandelon is almost universally adopted. It consists essentially of dissolving one part of mercury in ten parts of nitric acid having a specific gravity of 1.40 by the aid of gentle heat, and as soon as the solution is complete and has attained a temperature of  $54^\circ \text{C}.$ , it is poured into a flask containing 8.3 parts of alcohol of specific gravity 0.83. In most factories the following rule of thumb holds: Solution of 1 part of mercury in 1 part of nitric acid (sp. gr. 1.380) to 10 parts of alcohol. The mercury is dissolved in a glass carboy, and the solution poured into a second carboy containing the alcohol, which is connected with a series of receivers (Wolff) placed in a trough filled with water. The last receiver is connected with a chimney or condensing tower.

The reaction begins slowly with the development of whitish fumes, but very soon becomes quite violent, the liquid boiling and evolving copious white vapors of carbonic acid, nitric ether, acetic ether, etc., and finally the reddish-brown vapor of nitric oxide. The vapors are condensed in the receivers, and subsequently distilled with slaked lime, and the distillate, which is essentially an ethereal solution containing a large percentage of aldehyde, is used again instead of alcohol in making the fulminate. The reaction lasts between one hour and a half to two hours, at the end of

which time the supernatant solution is decanted from the fulminate and rain-water substituted. The contents of the carboy are next poured upon a cloth filter stretched upon a wooden frame and washed repeatedly until the wash-water no longer shows the slightest traces of acidity. The filters are then placed in the open air, protected from the direct rays of the sun, and the fulminate allowed to dry until it contains about 15 per cent of moisture. It is then packed in papier-maché boxes containing about 8 grammes each. In some factories it is stored entirely under water.

**Properties of Mercury Fulminate.**—The color of mercury fulminate varies from almost pure white to a dirty gray, depending upon the presence of very fine unconverted particles of metallic mercury intimately mixed in the mass. It may be purified by dissolving in boiling-hot distilled water, allowing the solution to settle and clear, and then decanting the supernatant liquid, from which, upon cooling, the fulminate crystallizes out in yellowish-white silky crystals. These crystals under the microscope appear to consist of two sets, the larger being octahedra with smaller orthorhombic crystals entangled and twined along the vertical axis. Mercury fulminate has a density of 4.42; it has a sweetish acid metallic taste, and, like all the compounds of mercury, is highly poisonous. Its most important property is its extreme sensitiveness to heat and shock of every kind. Its heat of formation (for one equivalent 284 grammes) is  $-62,900$  calories. Its heat of combustion in an inert atmosphere is  $+116,000$  calories for constant volume, and  $+114,500$  for constant pressure. This quantity of heat would be sufficient to raise the temperature  $4200^{\circ}\text{C}$ . Its heat of combustion in air is  $+250,900$  calories; the reaction attending its decomposition may be represented as follows:



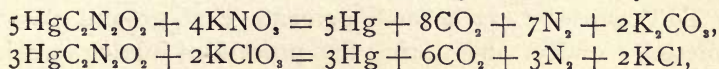
According to this equation one gramme of the fulminate should yield 235.8 c.c. of gas. Berthelot and Vieille have verified this several times, obtaining 234.2 c.c. Therefore

one equivalent (284 grammes) would furnish 66.7 litres of gas at 0° C. and 76 cm.

From the above equation it is seen that mercury fulminate, when detonated, does not give rise to the formation of any substance capable of undergoing a notable dissociation, consequently no gradual recombination can take place during the cooling which would retard the expansion of the gas and diminish the violence of the initial blow. This explains the brusqueness of the explosion, which would be all the more violent but for the condensation of the mercury vapor.

Dry mercury fulminate explodes violently when struck, compressed, or rubbed between hard surfaces; or when touched with concentrated sulphuric acid, or an incandescent wire, or any ignited body. If it be heated slowly, it explodes at 152° C., or, if heated rapidly, at 187° C. according to Hess, and at 200° C. according to Leygue and Champion. Ignited when unconfined it detonates with only a faint puff, but with only a piece of paper over it its force is developed in a marked degree. It is readily exploded by blows of metal upon metal, but with difficulty between wooden surfaces. It is claimed to be inexplusive when saturated with water, or if a particle of wet fulminate be exploded, the detonation is not communicated to the rest of the mass. There is no doubt but that its explosibility is reduced by moistening, and this property is utilized in reducing the danger inherent in handling large quantities of fulminate; but, on the other hand, explosions have been reported during the process of manufacture while the fulminate was still in the conversion-flask. Whether mercury fulminate explodes sympathetically or not is yet a matter of doubt. Attempts have been made to regulate the action of this explosive by mixing it with various substances, notably potassium nitrate and chlorate.

When mercury fulminate is mixed with potassium nitrate or chlorate and exploded, the following reactions may occur:





the first of which evolves +227,400 calories and the second +258,200 calories, the heat evolved here being double that from the pure fulminate, but the initial blow is tempered here by the phenomena of dissociation, due to the carbon dioxide, which renders these explosive mixtures less brusque in their effects. The temperature is also reduced at the outset by the distribution of the heat among the more considerable mass of products.

In addition to these salts of potassium, other substances are added to the fulminate in making percussion-caps and detonators, in which industry it finds its greatest practical use.

**Percussion-caps and Detonators.**—Caps and detonators are small cylinders made generally of copper and filled with an explosive composition. The size of the cylinder depends upon the purpose for which the cap or detonator is used, caps used in priming small-arm ammunition being about 2 mm. in length by 5 mm. in diameter, while the ordinary blasting-cap or detonator varies from 16 to 45 mm. in length and from 5 to 7 mm. in diameter. The copper cylinders are made in a single piece by means of a "punch-and-die" machine, and before being charged are carefully cleaned with gasolene, dried, and polished.

Formerly various substances were used in cap compositions, such as potassium nitrate and chlorate, sulphur, meal powder, phosphorus, antimony sulphide, etc. Saltpetre, sulphur, and phosphorus are no longer used. For ordinary gunpowder priming a very good composition consists of:

Mercury fulminate.....	37.5 parts
Potassium chlorate ....	37.5 "
Antimony sulphide.....	25.0 "

The mixture used in ordinary blasting-caps consists of:

Mercury fulminate.....	75 parts
Potassium chlorate ....	25 "

To these mixtures a small percentage of ground glass is sometimes added, and during the process of mixing, a solu-

tion of gum is used to give greater coherence to the mass and at the same time reduce the danger.

The manipulation of mercury fulminate is attended with very great danger, and the greatest caution is required in mixing cap compositions. Two processes are followed, known as the dry and wet. The former requires special machines, while in the latter case the ingredients are moistened with a solution of gum arabic in alcohol (more rarely shellac or gum benzöe are used), and then incorporated with a wooden pestle in a wooden or porcelain mortar. After incorporation the composition is put into the caps either wet or dry. When charged wet the caps containing the composition are placed in the "dry-house" and allowed to stand until the moisture has been driven off, the composition is then compressed and covered with shellac varnish, or a piece of very thin German silver, copper-foil, or paper. When made for use with time fuse the mouth of the cap or detonator is left open to receive the end of the fuse. In the case of electric fuses (or detonators to be fired by electricity), after the composition has been compressed, the open end of the cylinder is closed by means of a plug made of sulphur and ground glass, through which the wires pass and extend for about 3 or 4 mm. The ends of the wires are connected by means of a very fine wire so as to complete the circuit, and around this connecting wire (or "bridge") is wound a wisp of guncotton.

Detonators are graded according to the amount of fulminate they contain, and are known commercially as single, double, treble, quadruple, and quintuple force caps, the single-force cap containing three grains of fulminate, and the others increasing regularly by three grains.

The U. S. Navy detonator used in the torpedo service is an excellent example of an electric fuse, is more powerful than any trade detonator, and differs somewhat in other particulars. It consists of a copper case made in two parts. The lower part is a No. 38 metallic cartridge case, and is  $1\frac{1}{8}$  inches long and  $\frac{1}{2}$  inch in diameter. The upper part is a copper tube, open at both ends,  $\frac{5}{8}$  inch long and  $\frac{1}{2}$  inch in

diameter. A  $\frac{3}{16}$ -inch thread is cut on each of these parts so that the upper part screws nicely on the lower. The lower part is filled with fulminate of mercury (35 grains) up to the lowest thread of the screw. The upper part is fitted with a plug of sulphur and glass, through which the detonator legs pass to connect the bridge with the wires leading to the battery. When the fulminate is dry the spaces in the lower case and the caps are filled with pulverulent dry guncotton, and then the parts are screwed together.

Detonators are generally packed in tin or varnished cardboard boxes lined with felt, and the interstices filled with sawdust.

Practically blasting-caps may be tested by fitting a cap in a cork so that the base of the cap is just flush with the bottom of the cork, and firing it on a sheet of Swedish iron supported at its four corners. A good cap should blow a clean hole through No. 14 A. W. G. iron.

**Silver Fulminate.**—Silver fulminate has a composition similar to that of the mercury salt, the acid hydrogen of fulminic acid being replaced by silver instead of mercury. Its composition therefore would be represented by the formula  $\text{Ag}_2\text{C}_2\text{N}_2\text{O}_2$ .

Silver fulminate may be prepared in the laboratory as follows:

Introduce into a flask, of about 300 c.c. capacity,

Silver (granulated).....	1 part
Nitric acid (sp. gr. 1.308).....	20 parts

and shake gently until all of the silver is dissolved. Pour the solution thus obtained into a flask (2000 c.c. capacity) containing

Alcohol (87 per cent) .....	27 parts
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Bring the new solution to a temperature of  $212^\circ\text{F}$ . by placing the flask in a vessel containing boiling water, to which additional water is added as long as the reaction continues.



As soon as the solution becomes turbid, remove the flask, allow it to cool, and add

Alcohol (87 per cent)..... 27 parts

and replace the flask in boiling water. When the reaction ceases entirely, remove the flask, allow it to cool, and wash the opaque white crystals, until the decanted wash-water shows no traces of acidity. This process, so simple as described, requires the greatest care and caution. All danger of the liquid boiling over must be eliminated by the use of capacious vessels. All flame must be removed to a distance lest the vapors should take fire. The mixture must be stirred carefully, and, when dry, contact with hard surfaces must be avoided. It is generally transferred by means of paper shovels, and stored in pasteboard or paper boxes, or, if put in glass bottles, they should not be stoppered, but the mouth should be closed by a piece of paper with a sheet of rubber over it.

Prepared as above described, silver fulminate forms small, white, opaque, shining needles, having a strong bitterish metallic taste, and is very poisonous. It is but slightly soluble in cold water, but dissolves in 36 parts of boiling water and separates on cooling. It dissolves much more freely in aqueous ammonia, and is left behind unaltered as the ammonia evaporates. When exposed to white or blue light it gradually blackens, giving off carbon dioxide and nitrogen, and leaving a black substance mixed with a small quantity of the decomposed salt. It explodes much more violently than the mercury salt, and under the same conditions. When dry, it explodes at a temperature of  $130^{\circ}\text{C}$ . In a moist state it requires a much harder blow to explode it than when dry, but it can be made to explode, even under water, by friction with a glass rod. When well washed, and exposed to the sun until thoroughly dry, it explodes upon the slightest touch. Except in the manufacture of detonating toys, where very minute quantities are used, this salt is practically useless.

*Gold Fulminate* is a violently explosive buff precipitate formed by adding ammonia to the terchloride of gold.

*Platinum Fulminate* is a violently explosive black precipitate formed by mixing ammonia with a solution of binoxide of platinum in dilute sulphuric acid.

*Zinc Fulminate* is obtained by leaving zinc and water in contact with mercury fulminate, and allowing the solution to evaporate.

*Copper Fulminate* is obtained by boiling copper with water and mercury fulminate. It appears in the form of green crystals, which explode violently when heated.

In addition to these salts which are formed by the replacement of all the hydrogen in the original fulminic acid by a single metal, there is another class of fulminates, which are known as *double fulminates*, in which one half of the hydrogen is replaced by one metal and one half by another.

*Double Fulminate of Silver and Ammonia* is obtained by dissolving the silver salt in warm ammonia. Its composition may be represented by the formula  $\text{Ag}(\text{NH}_4)\text{C}_2\text{N}_2\text{O}_2$ . This double fulminate is more violently explosive than any of the single salts, and is exceedingly dangerous, even when moist.

*Double Fulminate of Silver and Potassium*,  $\text{AgKC}_2\text{N}_2\text{O}_2$ , is obtained by adding potassium chloride in excess to the fulminate of silver.

In considering the subject of the fulminates, certain other substances which, like the salts of fulminic acid, undergo, under normal conditions, a detonating explosion *only*, may very properly be included.

**Nitrogen Chloride or Chloramide.**—From a chemical standpoint this is the simplest example of a detonating substance, as well as one of the most unstable of explosive bodies.

This substance was discovered in 1811 by Dulong, "who, notwithstanding the fact that he lost one eye and three fingers in the preparation of this body," yet continued the investigation of the substance. The composition of nitrogen chloride had not yet been accurately determined. It is formed when

chlorine is led into a warm solution of sal ammoniac, or when a solution of hypochlorous acid is brought into contact with ammonia. From these methods of formation it would appear that the chloride of nitrogen is formed by the replacement of the hydrogen of ammonia by chlorine, but whether this replacement is partial or complete is an undecided question.

If we consider the replacement to take place by degrees, then three compounds would result according to the amount of chlorine substituted, thus:

$\text{NH}_2\text{Cl}$ .....	monochloramide
$\text{NHC}_2\text{Cl}_2$ .....	dichloramide
$\text{NCl}_3$ ....	trichloramide

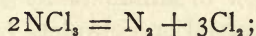
Nitrogen chloride may be conveniently prepared by inverting a bottle of chlorine, perfectly free from greasy matter, over a leaden dish containing one part of ammonium chloride in twelve parts of water. Great care is required to obtain the chlorine in a very pure state, and the gas must be dried before it is collected by passing it through sulphuric acid.

Nitrogen chloride, or the *trichloramide*, is obtained in the form of a heavy, yellow, oily liquid (sp. gr. 1.65), which volatilizes very easily and yields a vapor of characteristic odor which affects the eyes. Heated to  $93^\circ \text{C}$ . it explodes violently, emitting a loud report and a flash of light. Its instability is due to the feeble attraction with which its constituent elements are held together, and the violence of the explosion to the sudden expansion of a small volume of the liquid into a large volume of nitrogen and chlorine, and, possibly, hydrogen chloride. The explosion of this substance is at once caused by contact with substances which have an attraction for chlorine, such as phosphorus and arsenic; the oils cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently, while acids having no action upon chlorine are not so liable to cause



explosion. It has been distilled in the open air at  $71^{\circ}\text{C}$ . without explosion.

The decomposition of the trichloramide may be represented by the equation



therefore one equivalent (120.5 grammes) will furnish 44.65 litres of gas, or one kilogramme will yield 370.5 litres.

On account of its constitution and properties, this substance is of great interest in the study of explosives, although practically it is perfectly useless. It differs from all other explosives heretofore considered in that it contains no oxygen, and among the products of explosion we find only elementary substances. From these facts it would appear impossible that the explosion could result from combustion. This phenomenon has been thoroughly investigated, but only within comparatively recent years has any explanation been offered that seemed satisfactory.

This substance has already been referred to under the subject of thermo-chemistry.

Nitrogen chloride is a remarkable example of the endothermous class, and its extreme instability and explosiveness is explained as follows:

By observing the reaction which has been assumed to represent the decomposition of trichloramide, it is seen that the nitrogen atoms unite with each other to form molecules of nitrogen gas, and the chlorine atoms unite in a similar manner to form molecules of chlorine gas, and the amount of heat evolved by the union of these similar atoms so far exceeds the loss of heat that attends the separation of the dissimilar atoms of nitrogen and chlorine, that the decomposition of this compound is attended with the evolution of 38,100 gram-units of heat.

**Nitrogen Iodide or Iodoamide.**—This body may be made by dissolving iodine in the least possible quantity of alcohol (95 per cent) and precipitating it by pouring it into a

large volume of water. The finely divided iodine thus obtained is washed several times by decantation, and then gently triturated in a porcelain mortar with a large excess of concentrated ammonia water at  $0^{\circ}$  C. for several minutes, and the liquid poured off from the subsiding black powder. The ammonia is replaced two or three times by a fresh solution, and the powder is then transferred to a flask and washed thoroughly, first with alcohol (95 per cent), then with absolute alcohol, and finally with anhydrous ether, all of these liquids being artificially cooled. After the last washing, the ether is decanted until only a fluid black mud remains, which is poured upon a filter, drained a few moments, and the remaining traces of ether removed as vapor by means of a current of cold air.

On account of its extreme sensitiveness, iodoamide is made only for experimental purposes, and to avoid accidents it is advisable to divide the filter with the moist precipitate obtained as above upon it into small pieces, and expose them to warm, dry air at some distance from each other.

Iodoamide is a brownish-black soft powder, which when dry explodes from the slightest cause, producing a loud report, and destroying everything that may be near it. The explosion is attended with a faint flash of violet light, nitrogen being set free as gas, and iodine in the form of a very fine powder. It may be exploded by friction, even under water, and in the dry state it detonates upon being touched with a feather, or scratched with the edge of a piece of paper. When moist it decomposes slowly in contact with the air, yielding nitrogen, iodic and hydriodic acids, while under water it undergoes decomposition in the presence of a beam of light. Like the chloride, the composition of nitrogen iodide is still a question, Colin and Gay-Lussac holding that its formula should be  $\text{NI}_3$ , while others claim that it contains more or less hydrogen.

**Nitrogen Bromide or Bromamide**, whose composition is probably analogous to that of the chloride, may be formed by decomposing nitrogen chloride with an aqueous solution



of potassium bromide. It exists as a dense blackish-red, very volatile oil, having an odor like the chloride, and explodes violently by contact with phosphorus and arsenic.

**Nitrogen Fluoride or Fluoramide** is produced by passing an electric current through a concentrated solution of ammonium fluoride, and is deposited as oily drops on the negative plate. These drops explode violently when brought into contact with the positive pole, or with glass, silica, or organic matter.

**Silver Amine.**—This substance was discovered by Berthelot nearly one hundred years ago by acting on silver oxide with ammonia.

The formula for silver amine has been shown to be  $\text{Ag}_2\text{N}$ . It explodes upon the slightest shock when dry, and even when wet it requires the greatest caution. It is supposed to have been the initial detonating agent in the bomb that killed the Czar.

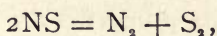
**Copper Amine, or Cupricamine.**—This is the copper compound similar to that just described, and is supposed to have the composition  $\text{Cu}_2\text{N}_2$ . It is formed by passing a current of dry gaseous ammonia over finely powdered cupric oxide heated to  $250^\circ\text{C}$ .; water and nitrogen gas are evolved, and the nitride is left as a dark green powder, which when heated to about  $310^\circ\text{C}$ . explodes feebly, emitting a red light. Strong acids decompose it with the evolution of nitrogen.

**Mercury Amine.**—By passing dry ammonia gas over the dry yellow mercuric oxide as long as the gas is absorbed, and then heating the resulting black-brown mass cautiously at a temperature not exceeding  $150^\circ\text{C}$ . until water ceases to be given off, this substance is obtained. It detonates powerfully when struck or heated, and is decomposed by acids into the salts of ammonium and mercury.

**Nitrogen Sulphide.**—This compound may be obtained by passing dry ammonia gas through a solution of sulphur dichloride in 10 or 12 times its volume of carbon bisulphide, until the brown color of the precipitate first formed disappears.



The yellow liquid is filtered from the ammonium chloride which is produced, and allowed to evaporate spontaneously, when the crystals of nitrogen sulphide are formed, mixed with sulphur. The sulphur is dissolved out by carbon bisulphide. It appears in the form of golden-yellow crystals of sp. gr. 2.22, and detonates powerfully under percussion, but is less sensitive than mercury fulminate. It deflagrates at  $207^{\circ}\text{C}.$ , is not affected by dry or moist air, and has been heated to  $50^{\circ}\text{C}.$ , without undergoing change. It irritates the mucous membrane of the nose and eyes painfully, although it possesses but slight odor. It is an endothermous body, and when decomposed according to the reaction



it evolves 31,900 units of heat.

In concluding this lecture there remains to be mentioned one other class of explosive compounds whose mode of action allies them closely to those which have just been described, and some of which are so highly explosive that they have been proposed for use as detonating primers.

This class is known as the *azo-compounds*, and are intermediate between the nitro-substitution and the amido-compounds.

Diazo-benzene may be considered as a type of this class, and may be formed by the indirect substitution of nitrogen for hydrogen in benzene. It is a quite unstable substance, while the nitrate, which is employed in the arts for the manufacture of dyestuffs, is so explosive that it has been proposed for use as a detonating primer.

According to Berthelot and Vieille, diazo-benzene nitrate is the residue of two nitrogenized bodies which have lost, the one (nitrous acid) its oxygen, the other (aniline) a part of its hydrogen, in the act of combination; but a notable portion of the energy of these elements remains in the residue, which accounts for its explosive character. If preserved in dry air out of contact with the light, this substance can be kept for

two months and more, but exposed to daylight it slowly changes; in moist air the change is rapid, and in contact with water it is immediately decomposed. When heated to about  $90^{\circ}$  C. it detonates violently; heated slowly at a lower temperature it gradually decomposes.

As a result of his "Researches on the Diazo-compounds," P. Greiss has obtained the paradiatriazobenzene, which explodes with extreme violence, when heated above its melting-point; metamidotriazobenzoic acid, which detonates when heated in the dry state; and metadiatriazobenzoic acid, which when heated explodes with the formation of a black cloud.

Finally, *silver hydrazoate*, a derivative of hydrazine— $N_2H_4$ —has been very recently proposed as a substitute for mercury fulminate, but as yet its properties are but little understood.

## LECTURE XIX.

### MANIPULATION, STORAGE, AND TRANSPORTATION OF HIGH EXPLOSIVES.

**Precautions to be Observed in Handling High Explosives.**—The danger of careless handling of explosives has already been alluded to, and cannot be too strongly emphasized. Modern high explosives are justly claimed to be safer to handle than gunpowder, but there are certain rules which cannot be violated with impunity. The tremendous power developed by the explosion of even a few ounces of these explosives renders the occurrence of small accidents highly improbable; and those whose duty it is to work with them should remember that *no margin is left for ignorance, carelessness, or stupidity*. The very safety of the new explosives seems to lead those who have had little experience with them into over-confidence, and for all who are called upon to deal with these substances practically, it is well to remember always that “*the function of an explosive is to explode.*”

The properties of the various modern high explosives have been enumerated, and the particular danger inherent in each. It is therefore scarcely necessary to add further words of caution with regard to handling them, and preparing them for use other than to insist upon proper respect being paid the tremendous power stored up in these substances.

In making or testing explosives in the laboratory, be sure that you understand thoroughly the several steps before undertaking the experiment, and during the investigation use only so much as is absolutely necessary to attain your object.



Often one gramme will answer your purpose far better than a pound, and with a correspondingly smaller disaster in case of accident. In using high explosives in blasting, or similar practical operations, deal with only the amount required for immediate use; for instance, it is not necessary to use more than a half-cartridge of dynamite in preparing a primer, therefore do not use a larger amount for that purpose. Do not stand over a box of dynamite or other explosive when preparing a primer; and when firing a charge be sure that the supply of explosives required for immediate use is well protected from the flying débris. Never carry detonators in the same basket, cart, or wagon with the explosive.

In using detonators with explosives of the "Sprengel Class," in which nitric acid enters as a principal ingredient, *it is absolutely necessary to prevent the copper case of the detonator from coming into contact with the acid*, otherwise a premature explosion is sure to occur. To avoid such accidents, coat the copper capsule thoroughly with paraffin by dipping it in a vessel containing melted paraffin, examining the coating afterwards to be sure that there is no break in its continuity.

Nitroglycerine compounds must never be exposed to shocks or violent compression between two metals. The danger attending the thawing of frozen dynamite has been alluded to, and the proper manner in which the frozen substance may be restored to its plastic state. It is to be noted that while frozen dynamite is less sensitive to ordinary shock, friction, and percussion than when in the unfrozen state, the reverse is true with regard to explosive gelatine.

In case of failure of a charge to explode, or to explode at the proper time ("hang-fire" as it is technically termed), do not hurry in seeking for an explanation for such failure. If after waiting sufficiently long (depending upon length of fuse and other attending circumstances) no explosion occurs, an examination may, and generally should, be made. If the exact depth of the tamping be known, it will generally suffice to remove the tamping to within a couple of inches of the charge, insert a new primer, retamp, and repeat the attempt

to detonate the charge. *In no case attempt to remove the charge.*

Always separate the tools used in drilling, boring, or other preparation for a blast from the explosive and detonators, and thereby prevent the repetition of accidents so often caused by dropping a drill, hatchet, or other tool.

Never permit smoking in the vicinity of the spot where a blast is in process of preparation. Finally, before firing a blast, be sure that every one is well beyond the danger zone, and protected from flying débris.

It is not within the scope of these lectures to enter into the theory of blasting, and those who desire extended information on the subject must have recourse to the various treatises readily procurable.

For such limited practical work with high explosives, however, as may be required of an officer in the ordinary performance of his duty, the following suggestions will prove of value:

**Manipulation of High Explosives in Preparing a Charge.**—As already stated, dynamite is usually supplied in the form of cartridges, but it may happen that for special reasons, such as for loading torpedoes, submarine mines, etc., it is delivered and stored in bulk. In such an event it may become necessary to prepare cartridges, which may be done as follows:

**How to Make a Dynamite Cartridge.**—The case may be made by cutting stiff brown manilla paper into rectangular sheets about five by eight and one-half inches, and rolling these sheets around a wooden mandrel of the required diameter, gluing the last fold, and turning in one end of the paper cylinder thus made. The case is next dipped two or three times into melted paraffin and allowed to dry. The granulated dynamite is weighed out and introduced into the case, and gently compressed by means of a wooden tamper, and the open end turned in until the cartridge is required for use.

**How to Prepare a "Primer" to be Fired by Means of a "Time-fuse."**—Dynamite is fired preferably by means of

a detonating-cap containing mercury fulminate. The cartridge to which the cap is attached is technically known as the *primer*. When electricity is not available, the usual method of firing a charge is by means of so-called safety or time fuses. One of the best fuses of this kind is made by Messrs. Bickford & Company, and consists of a core of meal-powder tightly compressed and spun around with yarn impregnated with water-proof composition.

Safety-fuses are known as "single-" and "double-tape" fuses, the former being used ordinarily, but the latter should be used when the primer is to be placed in damp places.

Before using a safety-fuse, its rate of burning should be carefully determined by attaching different lengths of the fuse to blasting-caps, and noting the time necessary for the powder-train to explode the caps. Having noted the rate of burning per foot of fuse, the next step is to cut off a length of the fuse, which when ignited will allow the operator ample time to retire to a place of safety before the charge is exploded, and to attach it to the cap.

The cap is carefully examined to see that no particles of the sawdust in which it is packed remain in the open end, and the clean, square-cut end of the safety-fuse is inserted in the open end until it is in contact with the upper surface of the fulminate. The fuse should fit the cap snugly; therefore, if it be too large it is pared down, or if too small it is wrapped with paper until a close fit is secured. The upper end of the cap is next tightly crimped on the fuse, so as to secure the latter and prevent it from becoming detached. If the charge is to be placed in a very damp place or fired under water, the junction between the fuse and cap should be made water-tight by a coating of paraffin, tar, shellac, or similar substance. The primer is completed by attaching the cap and fuse to the cartridge. One end of the wrapper is opened, and with a round stick slightly larger in diameter than the cap open a hole in the centre of the cartridge and insert the cap, at the same time compressing the cartridge with the hand so as to bring the plastic dynamite into close contact with the



cap. The paper wrapper is then drawn around the fuse and tied securely with a string. The cap should be inserted into the dynamite only two thirds of its length, so as to avoid the possibility of the fuse setting fire to the cartridge before igniting the fulminate in the cap.

The primer is placed preferably in the centre of the charge to be fired, and always in contact with the charge. The placing of the charge depends upon circumstances, and is determined by the object of the blast in each individual case, no general rule being possible, save that it should always be located so as to produce the maximum effect. The location of charges in the work of hasty demolition will be considered later.

**How to Fire Dynamite Cartridges by Electricity.**—The use of the ordinary time- or safety-fuse for firing high explosives is attended with two very serious disadvantages:

1. The numerous failures to fire at all and frequent cases of "hang-fire," both of which, and especially the latter, are the cause of innumerable accidents.

2. The practical impossibility of securing the simultaneous ignition of several charges, by means of which double and even treble the effect is produced as when the same number of charges are fired consecutively.

Both of these disadvantages may be eliminated by using electricity to ignite the primer.

The primer is prepared to be fired by electricity in precisely the same manner as already described in the case of the time-fuse, except that the cap is entirely imbedded in the cartridge, and instead of tying the wrapper around the fuse the fuse-wires are doubled back and fastened to the cartridge by two half-hitches, which effectually prevents the cap from being dislodged. An electric outfit for use with high explosives consists of electrical fuses, connecting- or leading-wires, and an igniting apparatus.

**Electrical Fuses.**—Electrical fuses may be divided into three classes, viz. :

1. *Low Tension*, for use with strong electrical currents of low potential.

2. *High Tension*, for use with condensed sparks capable of jumping a sensible air-space.

3. *Medium Tension*, specially designed for magneto-electric machines which generate electricity characterized by a potential higher than the former and lower than the latter.

Although the three great classes are thus well marked, it by no means follows that a given variety of fuse can only be ignited by a particular kind of electrical generator. While this is true for some varieties, others may be fired by electricity under any of its characteristic forms.

For example, the Abel magnet-fuse, although belonging to the medium-tension class, is not unsuited to frictional machines, and it may also be used with voltaic currents of high electromotive force. As a rule, however, each of the three classes of generators should be provided with a fuse specially adapted to it.

The only essential difference between the three classes lies in the manner of causing ignition. The low-tension variety usually acts by the heating of a very fine wire uniting the insulated conductors and imbedded in a suitable priming. The second and third classes are fired by the passage of the electricity through a small break in the metallic circuit at this point, the spark igniting a sensitive priming; they differ from each other in the chemical composition and the electrical resistance of this priming.

Every electrical fuse suitable for use with explosive compounds should have: 1st, two insulated conductors for conveying the current; 2d, a plug to receive and firmly hold an end of each near to, but not touching, the other; 3d, a small priming suitably arranged for ignition at this point; and, 4th, a metallic cap, containing a detonating charge, usually of fulminating mercury.

The ordinary electric detonator (or fuse), as well as the U. S. Navy detonator used in the torpedo service, have been

already described, and may be taken as examples of medium-tension fuses, which are used almost exclusively at present.

The ends of the wires extending through the insulating-plug into the cap to which the "bridge" is attached are known as "detonator-legs," while the ends projecting outward are called "fuse-wires." The fuse-wires should always be well insulated, and not less than two feet in length.

**Connecting- or Leading-wires.**—The wires used to conduct the electricity from the igniting apparatus to the point where it is to be applied are called *connecting- or leading-wires*. Two lines are used, one known as the conducting-wire, which conducts the current to the point of application; the other, or return-wire, completes the circuit back to the igniter. Any wire that is a good conductor of electricity may be used; it is not necessary that it should be insulated, although it is always better that it should be so. If the connecting-wires are uninsulated, care must be taken that they do not touch each other (so as to form a short circuit) or the ground. It therefore becomes necessary to attach such wires to poles provided with insulators. For important work, and especially when used in military operations, in which all possibility of failure is to be eliminated as far as possible, thoroughly insulated connecting-wires should always be used. Everything considered, the best connecting-wires for electric igniting are a perfectly clean copper wire carefully covered with india-rubber. For short distances the cotton- and paraffin-covered wires answer very well.

In addition to these wires there is another which is still more convenient for military purposes. It consists of two wires separately insulated which are encased in an additional insulation so as to form a single wire. Unless the wires attached to the fuse are at least two feet in length it is well to join the connecting-wires to the fuse-wires through the interposition of the two other short wires; otherwise the ends of the connecting-wires will be constantly blown off.

If the blast is to be a very large or important one, the wires should be suspended from poles provided with insulators



as in the case with uninsulated wire; but for short distances the insulated wires may be stretched along the ground. For all ordinary work, such as the destruction of timbers, iron or steel rails, that would be undertaken in a hurried raid the wires may be most conveniently carried on a portable double reel, so that they can be laid or gathered in with despatch, and without danger of tangles and breaks.

**Igniting Apparatus.**—Various kinds of apparatus have been devised for firing electrical fuses, but since the almost universal adoption of medium-tension fuses the use of dynamo-electric or magneto-electric machines has superseded all others. One of the most serviceable and reliable of these machines and one to be particularly recommended for military purposes is the magneto-electric machine made by Messrs. Laflin and Rand. The *Magneto Machine No. 3*, which has been found to fulfil more of the necessary conditions of military service than any other form of igniter, is encased in a wooden case  $16 \times 8 \times 5$  inches in size and weighs  $18\frac{1}{2}$  pounds. The external parts of the machine consist of a leathern strap handle, two brass binding-posts or terminals for the leading-wires, and a firing-bar, which works vertically through the top of the box. The internal arrangement consists of a Siemens armature, which revolves between soft-iron prolongations of the cores of an electromagnet. The electricity thus generated is transformed by a commutator from an alternating to a continuous current. The circuit passes from the commutator-springs into the adjacent ends of the windings of the magnet. The back-strap ends of the windings of the two halves of this magnet are extended to the terminals for the leading-wires, and thence to a brass spring and collar, where, by platinum contact-points, they are joined together, thus completing an interior short circuit tapped by the fuse circuit as a shunt. The magnet is wrapped with 1.76 ohms of cotton-insulated copper wire No. 18 B. W. G., and the armature with 0.92 ohm of No. 21 of the same.

The novelty of the machine lies in the mode of giving

rotation to the Siemens armature, and of switching into the fuse circuit the powerful internal current thus induced. Both objects are accomplished by the firing-bar, which consists of a square brass rod  $14 \times \frac{1}{2} \times \frac{1}{2}$  inch, fitted with a wooden handle at one end. The other end passes down into the box. One side is provided with rack teeth engaging in a loose pinion fitted over the armature-spindle prolonged. A clutch holds the pinion to the spindle when the rod is descending, but leaves it free when the latter is raised, thus restricting the revolutions of the armature to one direction only. When the firing-bar reaches its lowest position, it strikes the brass spring forming part of the interior circuit, and if in rapid motion the shock breaks the circuit and thus shunts the current into the fuse circuit. In passing from the top to the bottom of the box the rod causes seven and one half complete revolutions of the armature, and if the movement be the result of a sudden and strong downward pressure this is enough to develop a powerful electrical current.

To use this igniter the ends of the connecting-wires to be attached to the machine are carefully cleaned, and attached to the terminals by unscrewing the thumb-screws, inserting the ends through the holes, and tightening the screws until they are in firm contact with the wires. The firing-bar is then withdrawn to its entire length, and when everything is ready the fuse and charge are ignited by forcing the bar home again by a swift, uniform downward pressure, care being taken that the bar is kept strictly vertical.

This form of igniter is very compact and strong, and not liable to get out of order except through very rough usage. It may, however, become temporarily deranged through two causes:

*First.*—Dust or some foreign substance may find its way between the platinum contact-points. By removing the screws that hold it in place the rear of the case may be removed and the trouble remedied by using a piece of fine emery-cloth.

*Second.*—Trouble may arise from the surface of the com-

mutator becoming tarnished. In order to cleanse it remove the rear of the case as before, and also the small pin near the lower end of the rack, and then withdraw the rack from the case. The works of the machine, with the shelf upon which they rest, are next partially removed from the case, and the springs which press upon the commutator and the yoke which holds in place the spindle upon which the commutator revolves are disconnected. The commutator may then be cleaned with a piece of emery-cloth.

Proper attention to these details and careful preparation of the wires and fuses save a vast deal of trouble, and cannot be too strongly insisted upon where success is absolutely necessary and time is to be saved.

**Precautions to be Observed in Firing High Explosives by Electricity.**—In order to reap the full benefit to be derived from the application of electricity to firing high explosives close attention must be devoted to certain details, especially to the preparation of the wires. As before stated, the fuse-wires should be at least two feet long, and if of lesser length they should be connected with the leading-wires through a coupling of two short wires, otherwise the ends of the leading-wires will be constantly blown off. If practicable, whenever the primer is to be placed in a bore-hole, the fuse-wires should be long enough to extend at least six or eight inches outside of the hole. The ends of the fuse-wires are prepared to be connected with the leading-wires by paring off two or three inches of the insulation and cleaning the bare ends of the wire with a piece of sand-paper. If the leading-wires be insulated, the ends are prepared in the same manner; if they be uninsulated, the ends are thoroughly cleaned by being rubbed or scraped so as to remove any dirt, rust, or other substance that might form a coating on their surface.

The fuse-wires are joined to the leading-wires by bending back the ends of the latter so as to form a hook and then twisting the ends of the former snugly around them. If the ground be very damp, or if the charge is to be placed under



water, it is necessary to use insulated leading-wires, and also to protect the junctions of the leading- and fuse-wires. This may be conveniently done by slipping pieces of rubber tubing over the ends of the leading-wires, and as soon as the junctions are made, sliding the tubing over the exposed places and tying the ends tightly with twine.

*Never connect the fuse-wires with the leading-wires until absolutely sure that at least one of the opposite ends of the latter is disconnected from the igniting apparatus.*

The fuse- and leading-wires having been connected, the primer and charge placed in position, and the operator having retired into a place of safety, *then, and not until then, should the terminals of the leading-wires be connected with the igniting apparatus.*

The ends of the leading-wires are cleaned, and attached to the brass binding-posts by unscrewing the thumbscrews, inserting the ends in the holes, and tightening the screws until they are in firm contact with the wires.

To fire the charge, the firing-bar of the apparatus is withdrawn to its full length, and then forced home again by a swift, uniform, downward pressure, care being taken that the bar is kept strictly vertical so as not to be bent. With proper attention to details, it is possible to fire fifteen charges in the same circuit simultaneously.

**Precautions to be Observed in Loading Shell and Torpedoes.**—Torpedoes and shell are charged as follows: The loading should always be done in light wooden buildings, well ventilated; the floor should be frequently swept, and the sweepings, including paper wrappings, should be burned in the open air. Extremes of heat and cold are unfavorable conditions. No acids or alkalis should be allowed near the explosives, and above all no fuses. The latter are as dangerous as matches in a powder-magazine.

No unnecessary fire must be permitted in the vicinity. It is true that small quantities of these high explosives ignite by a spark or flame, and burn away harmlessly; but the result is different if the quantity be large enough to give time for

the heat of the burning portion to raise the rest of the mass to the temperature of explosion. Disastrous accidents have been traced to this peculiarity as a probable cause; and it is therefore well to have no larger supply in the loading-room than is necessary for immediate use.

Particular care must be taken in loading torpedoes and shell that none of the material remains in the screw-threads. The funnels are made long enough to project entirely through the loading-holes; but examination in every case should be made to see that both the male and female screw are free from particles of dynamite, before attempting to close the can or torpedo. That none of the powder should be scattered about the floor or among the tools, is self-evident.

Any exudation of free nitroglycerine must be carefully avoided. It is not likely to occur at ordinary temperatures; but as with other oils, warmth promotes fluidity. For this reason a loaded torpedo must never be left exposed to a hot sun; the heat of the confined air rises to an extraordinary degree under such circumstances in a few minutes. Accordingly, the torpedo must be *placed in the shade*; or, if this be impossible, it must be *covered with blankets kept wet by frequent additions of water*.

Nitroglycerine which has exuded from its absorbent recovers all its dangerous properties, and this rule is therefore imperative.

If there be any chance that the temperature of the seawater may fall below 45° F., care must be taken in loading the torpedo, and especially in priming the fuse-can, that the dynamite is left loose without any packing. In this state it is certain to detonate when the fuse explodes; while if packed solid, as in cartridges, a failure might occur.

Special care is requisite that the fuses are *deeply embedded in the priming charge of the fuse-can*.

**Storage of High Explosives.**—If it can be avoided, gunpowder and high explosives should never be stored in the same magazine; nor for obvious reasons should high explo-

sives be stored within the main work of a fortification, nor within the radius of 500 yards of other buildings.

If any considerable quantity of these explosives is to be stored, it is advisable to erect a special magazine for the purpose in the most unfrequented place, and to mark it plainly so that its dangerous character may be recognized.

It is also advisable to store not more than 1200 or 1500 pounds of high explosives in a single magazine. Such an amount of explosives may be stored in a magazine 14 feet long by 9 feet wide by 9 feet high, interior dimensions.

The magazine should be as light as possible, consistent with the necessary strength. The use of wood in construction is recommended in preference to any other material, although corrugated iron or steel possesses the qualities of strength and lightness. The building should be ceiled throughout with a space between the inner ceiling and outer sheathing of not less than six inches. This space should extend overhead and under the floor as well as around the sides, and should be packed with sawdust or any form of cellulose. The use of cellulose sheathing-boards on the interior is also recommended.

The magazine should be closed with a tight-fitting door of double thickness. The magazine should be fitted with racks or shelves to receive the boxes and cases of explosives arranged along the sides, leaving a broad passageway, which should be kept scrupulously clean.

Every box or case of high explosives should be opened as soon as it is received at the post, and the condition of its contents examined, and noted in the magazine-book. If found to be in good order, strips of blue litmus paper should be placed in each box, and the top replaced and secured by screws. Before a box is placed in the magazine it should be given two thick coats of paint or shellac, to protect the contents from moisture, and should be properly marked as to the kind of explosive they contain, condition when examined, and date of examination. The boxes should be examined at



least once a month, the old litmus paper replaced by fresh strips, and the boxes turned over.

The floor immediately under the boxes should be covered with clean white sawdust to absorb any nitroglycerine which may exude, and in case of leakage the sawdust should be removed immediately and burned.

"Sulphur Solution," made by dissolving "flowers of sulphur" in a solution of sodium carbonate, should be kept on hand to decompose any nitroglycerine which may soak into the shelves or find its way through the sawdust to the floor. If different kinds of high explosives are stored in the same magazine, they should be placed in separate sections as far as possible. No acids should be allowed in or near the magazine, and *under no circumstances whatever should fuses, blasting-caps, or detonators be stored in the same magazine with high explosives.* The precautions enumerated for the care of gunpowder magazines apply with equal force to the storage of high explosives.

If the dynamite be in the form of cartridges, the boxes should be placed so that the *cartridges may never stand in a vertical position.* If not perfectly protected from moisture, dynamite cartridges undergo a material change in appearance during storage, and this change may lead those who are not accustomed to handle the explosive to an erroneous conclusion as to its condition. The change is due to the absorption of moisture in the body of the cartridge which dissolves the alkaline carbonate, and carries the latter to the surface of the wrappers, where it dries and forms a whitish deposit. This does not, however, seriously impair the condition of the explosive, which under these circumstances should be examined by removing some of the explosive from the wrapper and testing it as already described, since no clue can be obtained from the litmus paper.

*Guncotton* should habitually be stored in a thoroughly saturated condition, i.e., it should contain from 30 to 35 per cent of water. In this condition it is practically inexplusive. By thoroughly coating the boxes with a composition of

shellac and Stockholm tar dissolved in alcohol, and securing the lids snugly by screws, they may be made practically water-tight.

It is advisable to saturate the disks of guncotton when they are received, replace them in the boxes with strips of blue litmus paper on top and between one or two disks, and then secure the tops. The boxes should then be weighed, and their weight, together with the data on the boxes of other explosives, noted on them. At the monthly inspections of the magazine the boxes should be reweighed, and should there be any appreciable loss of weight between any two consecutive weighings, the disks should be removed, saturated with water, repacked, and fresh litmus paper placed in the boxes.

*Dry Guncotton* should not be kept in the magazine, but when required for primers the necessary number of disks should be taken out and dried. Wet disks of guncotton may be conveniently dried by passing a clean strong string through the detonator-holes, and suspending them from the ceiling of the magazine. A disk of guncotton of the usual size should weigh approximately 10 ounces when dry.

Although it is not usual to find nitroglycerine in a liquid state at military posts, the following suggestions as to its storage may be of service.

*Nitroglycerine* is usually stored in quantities of 45 or 50 pounds in earthenware crocks, copper cans, or tin cans which are paraffined on the inside, and provided with tubes passing vertically through the centre of the cans. When stored in crocks, the explosive should be covered with a layer of water, and the crocks placed in copper vessels to catch the nitroglycerine in case of breakage from any cause. The cans are closed by means of water-tight tops.

The cans or crocks should always be placed on the lowest tiers or shelves in the magazine, which should not be more than eight or ten inches from the floor. As in the case of other high explosives, nitroglycerine should be examined

monthly by testing the water in the crocks for acidity, or by suspending strips of litmus paper over the mouths of the cans. Should traces of acidity be discovered and there are means at hand, the nitroglycerine should be removed from the magazine and washed as already described; otherwise it should be destroyed, and *under no circumstances should an attempt be made to return it to the factory.*

*Detonators* may be stored in small buildings of similar construction to that recommended for the storage of high explosives, but such a building should not be located within 500 yards of any other magazine.

**Transportation of High Explosives.**—High explosives when properly made and packed are quite safe against any shock to be expected in ordinary transportation. This is no longer true, however, in case of explosives which have begun to decompose or leak, and an examination should always be made as to their condition before transportation, especially if they have been stored for any length of time. As in storage, so in transportation, high explosives should be protected from extremes of heat and cold. On steamships, they should be stored in a well-ventilated place, remote from the engine-room, preferably on deck, unless the journey is to be a prolonged one and there is reason to expect very hot or cold weather. In the former case they should be protected from the direct rays of the sun, and in the latter covered with straw and tarpaulins.

In transportation by railway it is well to cover the floors of the cars with straw; this precaution should be observed also in transportation by wagons, etc. The boxes containing the explosives should be packed so that there is no danger of falling, and in the case of cartridges the boxes should be placed so that the cartridges will lie on their sides. Whatever the means of transportation, they should be protected from water, and the locality, car, or wagon should be plainly marked *Explosives—Dangerous.*

Under no circumstances should percussion or detonating



caps, matches, or inflammable material of any kind be placed in the same car, wagon, or locality with high explosives.

The above precautions, together with such others as may be suggested in any particular case, will greatly reduce the danger incident to the transport of high explosives.

## LECTURE XX.

### THE APPLICATION OF HIGH EXPLOSIVES FOR MILITARY PURPOSES.

IT does not fall within the scope of these lectures to consider the extensive operations undertaken by military engineers which involve elaborate calculations and extend through long periods of time. For such work, large amounts of explosives are generally used, and careful preparation is made so as to accomplish only the object in view.

In the case of hasty demolitions, such as ordinary troops in the field may be called upon to execute, economy of time and absolute certainty of success are the principal factors, so that nicety of calculation and extensive preparation are precluded, the general rule being to be sure to use sufficient explosive to accomplish the object in view (using a high factor of effectiveness) and to place it so as to produce the most destructive effect.

**Conditions to be Fulfilled by a Military Explosive.**—For military purposes an explosive should satisfy the following conditions:

1. It should be very powerful.
2. It should be stable under considerable variation of climate.
3. It should be insensible to the impact of projectiles.
4. It should be plastic.
5. It should be susceptible of easy and perfect explosion or detonation.

The principal objects of hasty explosions executed by troops are felling trees; destruction of beams of wood, iron, or steel; demolition of bridges, doors, walls, buildings, etc.; the destruction of railway tracks, material in general, and incidentally the removal of temporary obstructions in waterways, etc.

**Felling Trees.**—It may frequently happen that trees are to be felled quickly, either to clear the space around a defensive work, or to strengthen a position by means of an abattis, or for various other reasons. For the rapid execution of such work, time and labor may be saved by the use of high explosives. To fell a tree, the charge may be located in one of three positions, viz.:

1. *The charge may be placed in a circle, around and on the outside of the trunk.*

In this case a necklace made by enclosing the cartridges, *placed end to end*, in gunny-sacking, canvas, stiff paper, or other material at hand, is attached to the tree at the distance above the ground at which it is desired to cut the tree. The primer is most conveniently placed at one end of the necklace. When guncotton disks or blocks are used, the necklace may be made by stringing them on a piece of stout twine or wire.

For a hardwood tree having a diameter of *one foot*, the charge is *three pounds of dynamite No. 1*, or other explosive of equal force; and for trees of other dimensions the charge varies as the *square of the diameter*.

2. *The charge may be placed on one side of the tree.*

In this case the charge may be placed in a sack and hung against the tree, or it may be placed upon a beam placed against the tree. The charge is calculated as in the preceding case, but should be one fourth greater than when the necklace is used.

3. *The charge may be placed in holes bored horizontally in the tree.*

The hole (or holes) is bored in the tree with a *wood auger* of one and one-half inch in diameter to a distance of two thirds of the diameter of the tree and at the required distance



above the ground. The explosive is placed in the hole and tightly compressed with a *wooden rammer* so that it completely fills the cross-section; the primer is next inserted, and the hole tamped with wet earth or clay.

The charge for trees of from 9 to 12 inches diameter should fill the hole to one third of its depth; for trees having a diameter from 20 to 24 inches, the bore-hole should extend three fourths of the diameter, and the charge should fill the hole to one half of its depth; for trees having a diameter greater than 24 inches, two or more holes should be bored and charged as in the last case.

The direction of the fall of the tree may be determined by securing a stout rope to the upper portion, and taking a strain on it before firing the charge.

**Destruction of Wooden Beams.**—Wooden beams, *squared*, such as are used in bridge timbers, etc., may be destroyed in any of the three ways described for felling trees.

If the beam is square, the charge is calculated by the same rules; if rectangular, and the charge is to be placed uniformly across the width of the beam, the charge may be calculated as follows: For a wooden beam 12 *inches wide*, by 6 *inches deep*, the charge of dynamite No. 1 is 10 ounces; for beams of other dimensions, the charge *varies as the width and the square of the depth*. Thus to break a beam 24 inches wide by 9 inches deep would require a charge of 45 ounces.

**Destruction of Iron and Steel Beams.**—Wrought-iron beams (or plates) having a uniform width of one foot are destroyed by charges calculated as follows, and placed uniformly across the beam: A beam (or plate) twelve (12) inches wide by one-half ( $\frac{1}{2}$ ) inch thick requires a charge of six (6) ounces; for beams (or plates) of the same width, but of varying thickness, the charge varies as the square of the thickness. For beams (or plates) of varying widths as well as thicknesses, whether separate or built up in the form of beams or girders, the charge is calculated by the formula

$$L = ch^2b,$$

in which  $L$  = the charge in pounds;  
 $h$  = the thickness of beam (or plate) in inches;  
 $b$  = the width of beam (or plate) in inches;  
 $c$  = the charging coefficient.

For dynamite No. 1,  $c$  has been determined experimentally as follows:

For solid wrought-iron beams,  $c = 0.18$ ;  
For riveted wrought-iron beams,  $c = 0.09$ ;  
For solid steel beams,  $c = 0.25$ ;  
For riveted steel beams,  $c = 0.12$ .

If the beam or plate be less than six inches in width, the charge is calculated as above, and placed obliquely across the beam. For built-up beams or girders the charges are calculated as above, and are placed according to the thickness of the different places in the cross-section, taken collectively.

**Demolition of Bridges.**—The charges for the destruction of the several parts of a bridge, whether of wood, iron, or steel, are calculated as just described. The location of the charge is very important, and depends upon several considerations. The most complete destruction is effected by placing the charge on the lower flange of the girder at the centre of the span, but it is often difficult to reach this point.

Practically the best place for the charge is upon the lower girders, near an abutment or pier, and at a point where the thickness of the plates is least. If the sections are uniform throughout the length of the bridge, or if it is impracticable to reach the lower girder, the charge should be placed at the centre of a span and upon the upper flange of the upper girder.

To destroy the *chains* of a suspension bridge, the charges should be placed in the alternate spaces between the plates of which the chain is composed. To destroy a six-inch *wire-rope* or *cable* of a suspension bridge requires about twenty

pounds of dynamite No. 1, care being taken to attach the charge very securely and closely to the cable.

**Demolition of Doors.**—To destroy a doorway, a charge of from twenty to thirty pounds of dynamite No. 1 should be enclosed in a bag or piece of canvas, and suspended from a nail, spike, or pickaxe driven in the middle of the door. To produce the same effect with ordinary black powder, the charge should be from two to three times greater, and placed at the bottom of the door and covered with earth. To destroy *palisades*, the charge is placed on the ground at the foot of the pickets, the cartridges end to end, and at about one pound per running foot.

**Destruction of Railway-tracks.**—To destroy a rail on a first-class railway requires from 10 to 12 ounces of dynamite No. 1, or guncotton, two ordinary cartridges of the former or a block of the latter forming a very convenient charge. The charge should be placed in close contact with the web of the rail, and if practicable secured in position, which can generally be done by taking a couple of half-hitches around the rail with the fuse-wires. The charge should also be tamped by covering it with earth.

For rails fixed in chairs, the charge should be placed in the chair. From two to three miles of track per hour may be effectually destroyed by a detail of eight men.

**Destruction of Artillery Material.**—Field-guns may be destroyed by firing a charge of two pounds of dynamite No. 1 attached to the chase near the muzzle and covered with a sod of earth. To destroy a siege-gun, double the charge and proceed as with the field-gun. Either gun may be destroyed by filling the bore two-thirds full of earth or sand, placing the above charges within the bore, and tamping with moist sand or earth to the muzzle and firing. In the latter case there is danger from flying pieces, or iron or steel.

If it is desired to break the piece up entirely or to destroy a gun of heavy calibre, it may be accomplished as follows: Plug the vent so that the gun is water-tight, and bury the piece muzzle upward, so that the muzzle is on a line with the



surface of the ground. The charge is calculated from the weight of the gun, at the rate of *three pounds per ton*, and is divided into two parts, one of which is double the other. The two parts of the charge are primed separately (but connected in the same circuit) and attached to a wooden rod, so that the greater will be at the base of the bore and the smaller slightly above the trunnions when the rod is introduced into the bore of the gun. The rod is inserted carefully into the bore, which is next filled with water (or earth), the muzzle closed with a wooden tompon, and the charges fired.

Gun-carriages, wheels, etc., may be destroyed according to the directions already given for the destruction of wooden beams, iron plates, etc.

#### **Removal of Temporary Obstructions in Waterways.**

—In addition to the hasty demolitions undertaken by troops, already enumerated, it sometimes becomes necessary to remove temporary or even permanent obstructions in waterways. To blast or cut off piles driven in a channelway or elsewhere in water, a convenient method is to attach the charge to a hoop and lower it into position by means of stout twine and weights, or by a pole, slipping the hoop over the pile. If a row of piles is to be attacked, the charge is conveniently attached to a horizontal pole instead of a hoop, and placed in position in the same way. The charge may be put in rubber or other water-proof bags, but it should be put preferably in tin canisters. The precautions as to the proper method of insulation, etc., have already been alluded to in a previous lecture. To completely cut off a pile from twelve to fourteen inches in diameter under water, requires a charge of one pound of dynamite No. 1.

Piles or stumps partially embedded in a river-bottom may be removed by attaching the necessary charge to the end of a long pole, and gradually and carefully placing the charge under or partially under the object to be loosened.

Sunken vessels are more difficult to remove, and require much larger charges of explosive. Masts may be cut away

at the deck as already described for piles. To destroy hulls, the charges should be placed in the interior of the wreck, if possible, and the services of a diver may be necessary. Should the water be not too deep, and the hatches be open, however, charges of twenty-five or thirty pounds of dynamite lowered into the hatches, fore and aft, will generally suffice to open up the hull completely, and the remaining wreckage may be destroyed as indicated.

In swift currents, the charges may be placed in iron pipes and lowered alongside of the wreck and fired, the pipes acting as anchors to hold the charges in position. When two or more charges are to be fired simultaneously under water, they should be placed singly, and the wires leading to each charge brought to surface and connected in the circuit very carefully. In all submarine blasting, it will prove economical, both as to time and expense, to use large charges so as to insure the full effect desired.

To remove ice so as to open navigation, dynamite may be advantageously used. In running water the operation should be begun in places where the loosened ice can be carried away by the current. By placing charges near the shore and covering them with earth, and proceeding from shore to shore with charges under the ice, the maximum effect is obtained. Vessels which have been blocked up in ice may be freed in a similar manner.

**Relative Force of Explosives.**—The formulæ by which the charges have been calculated in the preceding pages for the accomplishment of various kinds of work are purely empirical, and are true only for dynamite No. 1 and gun-cotton. When other explosives are used, these formulæ must be modified according to the relative strength of the explosive used. For that purpose the following table, which was established by means of the Quinan pressure-gauge, may be used:

Name of Explosive.	Compression of Cylinder.	Order of Strength.
I. Explosive gelatine ..... (Made from nitroglycerine after the Vonges process.)	0".585	106.17
II. Hellhoffite.....	.585	106.17
III. Nitroglycerine..... (Made Nov. 19, 1889, tested Jan. 6, 1890.)	.551	100.00
IV. Nobel's smokeless powder.....	.509	92.38
V. Nitroglycerine..... (Made Jan. 29, 1890, and tested on the same day. U. S. N. Torpedo-station proc- ess.)	.509	92.37
VI. Explosive gelatine ..... (Made from the last nitroglycerine.)	.490	88.93
VII. Guncotton..... (U. S. N. Torpedo Station, Lot 100, 1889.)	.458	83.12
VIII. Guncotton..... (Stowmarket, 1885.)	.458	83.12
IX. Nitroglycerine..... (Made according to the French process and tested on the same day.).....	.451	81.85
X. Guncotton..... (Made in Artillery School Laboratory.)	.448	81.31
XI. Dynamite No. 1.....	.448	81.31
XII. Dynamite de Trauzl.....	.437	79.31
XIII. Emmensite.....	.429	77.86
XIV. Amide powder.....	.385	69.87
XV. Oxonite..... (Picric acid fused before being added.)	.383	69.51
XVI. Tonite.....	.376	68.24
XVII. Bellite.....	.362	65.70
XVIII. Oxonite..... (Picric acid not fused.)	.354	64.24
XIX. Rackarock.....	.340	61.71
XX. Atlas powder.....	.333	60.43
XXI. Ammonia dynamite.....	.332	60.25
XXII. Volney's powder No. 1.....	.322	58.44
XXIII. Volney's powder No. 2.....	.294	53.18
XXIV. Melinite.....	.280	50.82
XXV. Silver fulminate.....	.277	50.27
XXVI. Mercury fulminate.....	.275	49.91
XXVII. Mortar powder ..... (Dupont.)	.155	28.13

**Champion's Experiments with High Explosives during the Franco-Prussian War.**—M. Champion, of the French Artillery Corps, furnishes the following valuable information, which he gathered during a series of practical trials in the siege of Paris by the Prussians.



*Destruction of Palisades.*—The palisade, which was constructed in view of the experiment, had a length of one metre, and was of the ordinary model.

At the base a cartridge containing five pounds of 50% dynamite was placed. The explosion destroyed all the stakes, and the fragments were projected in all directions.

Complete rupture of palisades of the ordinary model was produced by exploding cartridges charged with four pounds of dynamite, and suspended at their ends from the palisades. The same effect was also produced by zinc tubes containing five and a half pounds of dynamite per running metre, placed at the foot of the palisades.

In the first explosion, out of fourteen stakes, nine were cut at the height of the cartridge; five were injured more or less without being thrown down. In the second explosion, five stakes which were in front of the cartridge were cut away.

The fact was also established in the second explosion, that no splinters were thrown in the direction of the operator.

*Doors and Wooden Enclosures.*—Small cartridges, weighing three to four ounces, were hung up on nails along the walls, about four inches apart. By exploding one of them, the other cartridges exploded simultaneously along the whole line.

The weight of the cartridges varied with the thickness of the obstacles.

Tamping, in both cases, would diminish the quantity of explosive used, without modifying the result. Sacks of earth, or any débris can be employed for tamping.

*Trials on Walls.*—The third series of experiments was made on a wall two feet high and one and a half feet wide, constructed of rough-stone masonry, joined by good mortar, and forming regular layers in the lower part.

The wall, covered with a coping of flagstone, was very solid, and made of the very best kind of material, and could be considered as a very substantial structure.

A can containing three kilograms eight hundred grams of 50% dynamite was placed vertically at the foot of the wall, and the cap was introduced through the cork stopper, and

the charge fired. A gap of eighty centimetres wide and eighty-five centimetres high was opened at the foot of the wall. The same aspect of the opening was noticeable on both facings of the wall.

The rocks flew in both directions, so that with a small hammer it was enlarged to an opening of one metre fifteen centimetres high, and one metre seventy centimetres wide.

A second trial was made under the same conditions, but covering the can of explosive by four sacks filled with sand. The effect was notably increased; and the breach made was one metre seventy centimetres wide by two metres forty centimetres high, and the base of it was covered with rocks to a height of seventy centimetres. The wall was shaken to the top, and two metres fifty centimetres in width.

The sacks of sand were projected to a distance of twenty-five metres back of the explosive, and some bowlders were sent flying to a distance of sixty metres in front of it.

Therefore the tamping augmented very largely the effects of dynamite; but the weight of the sacks renders them inconvenient to carry, especially when in the presence of an enemy and when the work has to be rapidly executed.

In the third trial the object in view was to determine the most advantageous method for placing the dynamite can against the wall, without being obliged to cover it with sand. It was placed against the wall, on a slab about seventy centimetres high, and was fired without any other preparation.

The breach about fifty centimetres above the ground presented an opening of eighty centimetres in width and one metre in height on the face against which the explosive was placed, and one metre by one metre fifty centimetres on the opposite side.

The wall was also shaken two metres high and two metres wide, and the breach could be enlarged by hand. There is, according to this trial, a great advantage in raising the charge of dynamite about one third of the height of the wall, instead of placing it on the ground.

A fourth experiment was made to substantiate an experiment previously made by M. Champion.

He had established the fact that when a charge of dynamite is placed against one of the walls in the interior of a room only one breach in this wall is made, whereas the three others are thrown down; on the contrary, if the charge is placed in the middle of the room, the four walls would tumble down. The question naturally arose, if it would not be advantageous to place the charges at some distance from the wall which it was desired to destroy.

Four kilograms of dynamite, in two canvas sacks, were placed on a little earth-knoll about fifteen centimetres high and fifty centimetres from the wall, and surrounded by small sacks full of earth, but open against the face of the wall. The explosion produced only a small breach, fifty centimetres by fifty centimetres; but the wall was shaken up to its full height and three metres in width. The slabs on the coping of the wall were displaced. With very little exertion, and without tools, all the shaken part could be taken down.

Probably enclosure walls, which are generally of poor masonry, can be best destroyed in this manner.

The quantity of the dynamite charge should be in proportion to the solidity of the wall.

The less solidity a wall possesses, the more difficult it will be to throw it down, or to make a breach in it; as a bad wall gives way easily to the breaking effect of the explosion, and propagates the shock but little. The charge is therefore placed at a greater distance, and has a chance to act on a greater surface; and, owing to the bad construction of the wall, it will throw it down.

A fifth experiment was made.

In a box twenty-four centimetres by fourteen centimetres, four cartridges of dynamite were placed, each cartridge weighing seventy-five grams; and they were placed at one metre thirty centimetres above the ground. The explosion opened a breach sixty centimetres by thirty centimetres opposite the



charge, and seventy centimetres by ninety centimetres on the other side of the wall.

The shock also fissured the wall, so as to enlarge the opening to one centimetre by eighty centimetres, one metre above the ground. In fact, all the experiments were conclusive in favor of the employment of dynamite in preference to gunpowder, when it is desired to produce quick effects.

Its weight is very small as compared to that of powder required to produce the same effect, and the charge need not be tamped to give satisfactory results. Consequently, without fatigue, a sapper can carry to great distances all that is required to make a breach in a wall for giving passage to a whole regiment if necessary.

*Destruction of Walls at Buzenval.*—The enemy was intrenched behind the enclosure of the park. A first explosion produced a breach. The operation presented great difficulties. The men who had to carry the explosives were few in number. Nevertheless, some soldiers and men of the engineering corps volunteered under the directions of M. Pellet, and approached the indicated spots, and, by means of canvas sacks containing two kilograms of dynamite, made openings which permitted some soldiers to pass through. The walls were thin, and it was only necessary to fire the charges without tamping to open these breaches.

*Destruction of Houses.*—First. In a small dwelling at Drancy, about twelve feet wide, four kilograms of dynamite were placed inside the building and against the wall. Doors and windows were left open. The house was thrown down without projection of building material, and only the wall against which the dynamite was placed remained standing, although the walls were cracked and fissured.

Second. Stone cabin at Bobigny. Thickness of wall, thirty centimetres. Four kilograms 50% dynamite, the same as in the preceding example, were placed in a corner which seemed to offer the most resistance, opposite the door.

The cabin was completely destroyed, and the rocks went flying in all directions.

It is preferable, in destroying buildings, to place the charge in the middle of the room, as an even pressure is exerted on the surface of the exploding chamber; experience has confirmed this theory.

## LECTURE XXI.

### THE USE OF HIGH EXPLOSIVES IN SHELL.

AMONG the many practical uses to which high explosives may be applied for military purposes is that of bursting-charges in shell.

It hardly comes within the province of these lectures to consider the many special machines which have been devised to throw large masses of various high explosives contained in specially constructed projectiles, but a brief résumé of the attempts that have been made to fire either the ordinary or special shells from powder-guns may prove of material assistance to us.

**Experiments with Shell charged with Guncotton.**—Attempts to use guncotton as a bursting-charge for shell were made as early as 1864, when, under the direction of the English Guncotton Committee, twenty-five rounds were fired with unfused shell charged with dry, long-staple guncotton.

The first ten rounds were successfully fired from a 10-inch smooth-bore; the next ten rounds were fired from a 13-inch mortar with like success. But of the last five rounds, which were fired from a 7-inch B. L. Armstrong, two of the shells burst, one just beyond the muzzle, and the other (last) within the bore, and injured the gun to such an extent as to render it unfit for further service.

It was believed that these explosions were due to the compression or friction produced by the "setting up" of the comparatively loose charges at the moment of starting.

In 1867 experiments were resumed with compressed



pulped guncotton. Two steel shell compactly filled with disks of guncotton were fired from an 8-inch shunt-gun, the first bursting after one graze on the range, the second bursting in the bore, shattering the chase, and leaving nothing in front of the trunnions.

During the same series of experiments one round was fired from a 7-inch M. L. Woolwich gun. The shell burst in the bore, cracking and expanding the gun, which, however, remained entire. In these experiments ordinary shell were used, the only precaution observed being the wrapping and packing of the explosive.

In 1882 similar experiments were instituted in Germany to determine the possibility of using large charges of guncotton in projectiles for the 21-centimetre mortar. The shell were of cast steel with very thin walls and five calibres in length. Apparently these experiments were successful, since at present guncotton shell which are made in two parts are used in this mortar. These shell consist of a head and body which are secured together. The charge, which is enclosed in a zinc or iron box, consists of compressed guncotton disks 5 cm. thick and containing 20 per cent of water. The upper disk is provided with a cylindrical cavity to receive a primer of dry guncotton, which in turn is perforated to receive the detonator. When the charge is placed in the box a wooden rod is inserted in the detonator-hole, and melted paraffin is poured in to fill the insertion of the detonator. To load the shell the charge is introduced into the box as indicated, and the box placed in the shell and the head of the latter screwed on. A hollow screw is inserted in the eye of the shell to hold the box in place, and finally, immediately before being placed in the gun or mortar, the fuse and detonator are inserted in the aperture in the screw.

These projectiles have given good satisfaction, not only in the 21-cm. mortar, but also in the 15- and 28-cm. pieces.

This projectile is similar in nearly every particular to the one recently invented by Von Forster and Wolff, in which granulated guncotton is used.

The further record of experiments conducted by the German Government refers more to the action of the fuses used with shell charged with guncotton than to investigating the possibility of extending the use of such bursting-charges to guns of larger calibre and rifled pieces.

In this country, however, the importance of this latter line of investigation was recognized, and in 1884 Commander Folger, U. S. Navy, succeeded in firing fifteen rounds of guncotton at a range of 200 yards with the 80-pounder B. L. rifle, using full charges of powder. The shell were filled with guncotton saturated with water, and no precaution was taken to relieve the shock upon the first impulse beyond placing a layer of oakum one quarter of an inch thick in the base of the shell. In loading these shell the ordinary service disks were broken up in order to introduce the explosive through the fuse-hole; the density was consequently greatly reduced.

These experiments were followed by others, conducted at the U. S. Naval Torpedo Station, to test thoroughly the safety of the service guncotton as bursting charges for *fused* shell fired from service guns under service conditions. Unfortunately the only guns available for these experiments were Dahlgren 24-pounders and 20-pounder M. L. rifles.

Special shell were made for the tests. For trial with the 24-pounders they were of cast iron, fitted with base-plugs and ogival heads, and had an exterior diameter of  $5\frac{3}{4}$  inches, interior diameter of 5 inches, and length of 8 inches. The space between the disks and the walls of the shell was well filled with fine sawdust and rammed. Full service charges of powder were used in the tests.

In the first four rounds from this gun the shell charge consisted of three and one-half disks of wet guncotton, weighing  $4\frac{1}{2}$  pounds each, the loaded shell weighing 30 to 32 pounds.

The first shot was fired pointblank at the masonry escarpment of the fort on Rose Island, 50 yards distant from the muzzle. The shell was broken up and the guncotton scattered, but no explosion followed.

The second shot, fired under similar conditions, struck in the crevices of the masonry and buried itself in the earth behind the wall. It was recovered intact, except that a fragment was broken from the projecting base-plug, and was fired again (fourth shot) at the butt, the result being similar to that of the first shot.

The third shot was fired up the bay, and, although it ricocheted along the water, it neither exploded nor broke up.

The fifth shell was loaded with one dry and three wet disks; the sixth with two dry and two wet; and the remaining four were charged with four dry disks each.

These last shots were all fired into the escarpment, and, although the shell broke up on impact, there was no explosion, either in the gun, during flight, nor upon impact.

The shell used with the 20-pounder were made of four-inch steel tubing, one quarter of an inch thick, fitted with conical heads and movable base-plugs, and were of such diameter that the disks fitted them snugly without packing. The only precaution against the initial shock was the placing of an asbestos gasket over the base-plug. The full service charge of powder was used, and all other service conditions observed.

The first four shell were loaded with from 4 pounds 9 ounces to 6 pounds 6 ounces of wet service guncotton, and fired into the butt, with the result that there was no explosion; the shell, however, being distorted and crushed, but still containing some of the explosive, the rest being scattered around.

In the five following shots the shell were loaded with thin ( $\frac{1}{2}$ -inch) disks made by splitting the ordinary disks, and the guncotton was dry. The result of the fifth shot was identical with those preceding, but the last five shell broke up in the gun without explosion of the guncotton or damage to the piece.

These experiments were continued at the U. S. Naval Ordnance Proving Grounds, where six shots were fired from a 6-inch B. L. rifle. The projectiles were elongated shrapnel cases with movable heads. As in the experiments already



recorded, it was proven beyond a doubt that it was possible to fire shell loaded with guncotton, wet or dry, from the ordinary powder-guns, using service charges and under service conditions.

**Experiments with Shell charged with Nitroglycerine.**—During the year 1885 a curious and novel device of Mr. C. P. Winslow was tested by the Naval Ordnance Board. The device was a high explosive shell, so arranged that the bursting-charge—nitroglycerine—was to be made during the flight of the projectile, and fired upon impact, either by shock or by means of a specially prepared fuse.

The shell consisted of two glass jars, one within the other, the inner one containing a mixture of nitric and sulphuric acids in the proportions by volume of 4 : 3, and the outer one glycerine and sulphuric acid in the proportions of 6 : 1; the two jars containing equal volumes of the mixtures. These jars were fastened together by means of screw-caps and introduced into a tin cylinder, which in turn was placed within the shell proper. The shell itself consisted of two sections, which were securely joined after the cylinder containing the jars had been inserted. Rupture of the jars at the time of firing was prevented by transverse bars in the shell, to which the exterior jar was securely fastened by means of rubber bands.

To cause the shell to explode at any point of its flight, a time-fuse properly cut ignited a priming of rifle-powder, and forced a plunger contained in the rear section of the shell violently forward, thus breaking the jars. The rotation of the shell and broken glass were then supposed to mix intimately the contents of the jars, thus forming nitroglycerine, which was exploded by shock upon impact, or, if that failed, by means of a secondary charge of rifle-powder contained in an axial chamber of the plunger.

Experiments with this device proved very unsatisfactory, and the shell was condemned. In 1887 the Smolianinoff method of firing nitroglycerine from powder-guns was tested at the Naval Torpedo Station. The nitroglycerine was first

rendered insensitive by treating it with liquid, the character of which was kept secret, and then completely filling the shell with the explosive, and inserting a burster to which was attached a time-fuse. The 24-pounder howitzer was used, and twenty rounds were fired with the service charge of powder. The shell held from one to one and one-half pounds of the liquid, which contained 97 per cent of nitroglycerine.

Five shells were unfused and fired into a masonry wall, fifty yards distant from the gun, with the result that all were broken up, but apparently without explosion. The remainder were fired up the bay, and, with the exception of three, they exploded in midair at the time fixed, with a sharp report, scattering the fragments of the shell over a very wide area.

Previous to these experiments the inventor claimed to have fired, without accident or premature explosion of any kind, over 300 shells from a condemned 20-pounder Parrott rifle.

During the same year these experiments were repeated before the Army Ordnance Board at Sandy Hook with equal success. In these latter trials the shell, weighing from 82 to 89 pounds, and containing from 4.1 to 4.6 pounds of the prepared nitroglycerine, were fired from a 100-pounder Parrott rifle. At the conclusion of the Newport trials, the Navy Board reported that the Smolianinoff method of firing nitroglycerine from ordinary powder-guns was feasible, and recommended that further experiments be made to test its value for guns of greater calibre.

**Experiments with Shell charged with Dynamite.**—In 1867 shells charged with dynamite were successfully fired in Sweden from an 18-pounder howitzer with about two pounds of gunpowder. Three years later, during the winter of 1870–71, similar experiments were undertaken in Germany with a 6.8-inch Krupp gun. Shells fully charged with dynamite were fired without accident, using very small powder-charges, but when the latter was increased to 1.65 pounds the shell burst in the bore.

Two shells were successfully fired during the siege opera-

tions of the Second Corps of the Army of Versailles (1871), one from a 24-pounder howitzer, the other from a mortar. The dynamite was enclosed in a rubber bag held in position with gunpowder, and was ignited by time-fuses.

In 1874 Commander Barker, U. S. Navy, fired without accident of any kind at the Torpedo Station, nine shell charged with dynamite from a 24-pounder howitzer. Full service charges of gunpowder were used, and all service conditions as to the shell were observed. Three of the shell were unfused and were fired into the wall of an old bomb-proof, exploding upon impact. The remaining six were fused (Bormann) and fired up the bay, none exploding prematurely, and some of them at the fixed time. In 1884 experiments were made with firing dynamite from powder-guns, using a special form of shell designed by Mr. F. H. Snyder.

The shell consisted practically of a sabot, built up of gelatinized fibre, leather, and copper disks placed next to the powder-charge; next came a brass case containing a cellular rubber buffer, and then a wooden plunger for compressing the buffer, and finally the magazine for holding the dynamite.

These shell proved unsuccessful at the time, although the inventor claims to have overcome the difficulties and to have successfully fired shell charged with five pounds of dynamite. During the same year Commander Folger, U. S. Navy, fired 22 shell, each containing  $5\frac{1}{2}$  ounces of dynamite from a 12-pounder (10 rounds being fired under service conditions), the only precaution taken in loading the shell being a little oakum introduced as a packing.

In 1886 a shell designed by Mr. J. W. Graydon (at that time Lieutenant, U. S. Navy) was tested at the Presidio, San Francisco; 52 unfused shell containing dynamite No. 1 being fired from a  $4\frac{1}{2}$ -inch siege-gun, using the service-powder charge. These experiments were conducted before a Board of U. S. Army Officers appointed to investigate and report upon the invention, and were so successful that the board unanimously recommended that the trials be continued with



the 8-inch converted M. L. rifle and the 15-inch smooth-bore gun.

The shell was loaded and prepared for firing as follows: It was first lined with asbestos paper, two thicknesses being placed on the bottom, and the dynamite was then introduced in paraffined packages and rammed with wooden rammers until the shell was filled. Between the base of the projectile and the powder-charge were inserted eight asbestos wads. Experiments with this system were continued the following year by the Army Ordnance Board at Sandy Hook.

A 7-inch Ames M. L. rifle was used, and steel shell weighing 122 pounds, containing 2.3 pounds of dynamite No. 2, were fired with powder-charges of 23 pounds. These shell were fused and filled with base-plugs for convenience in loading. Seven shots were successfully fired at a section of a wrought-iron monitor turret at the distance of 110 yards.

**Experiments with Shell charged with Explosive Gelatine.**—In 1883 an Ordnance Board, U. S. Army, fired from the 3-inch wrought-iron field-gun five shell, each charged with  $6\frac{1}{2}$  ounces of explosive gelatine and fitted with Schenkle percussion fuses. All the shell burst after leaving the gun and before reaching the target. The explosive had been on hand for some time. These experiments were continued during the same year, the same gun, but a new lot of Nobel's explosive gelatine and new projectiles, being used. The first shell broke up on leaving the gun, and the second struck the target sideways and broke in pieces. Five other rounds were fired, and all of them broke up prematurely. It was thought that the want of success was due to the heat generated by friction between the rotating projectile and the explosive; therefore three projectiles were made for trial with the 3.2-inch gun, in which the difficulty was avoided, but with no greater success.

Further experiments were conducted with the 8-inch converted M. L. rifle. New cast-iron projectiles were made, having ogival heads which were connected to the body by means of screw-threads. To avoid friction between the explosive and the walls of the projectile, the explosive was packed

in a pasteboard cylinder divided longitudinally into four compartments by two pieces of wood. The cylinder fitted the shell loosely, and was coated on the exterior with plum-bago and tallow. The shell contained about five pounds of explosive gelatine, and the powder-charge consisted of forty pounds of Dupont S. H. powder. Between the gunpowder-charge and shell was interposed a hollow rubber buffer six inches long and one inch thick. The first and third shell broke up on impact, the second separating as it left the gun.

A new shell was next made and tested. In it the explosive was made to revolve with the projectile by means of a copper diaphragm let into grooves cut into the interior walls of the shell. This shell proved successful, but a heavier and stronger steel shell with a solid head and heavy screw base-plug destroyed the gun. At first this accident was attributed to the fact that the gelatine was old and uncamphorated, but a second round in which new camphorated gelatine was used also burst in the muzzle of the gun.

It is but fair to observe, however, that during these trials three Butler shell charged with gunpowder and fused with fulminate fuses broke in precisely the same manner as did those containing gelatine. Subsequent experiments with explosive gelatine as a bursting charge for shell fired from powder-guns have proved equally unsuccessful.

**Experiments with Shell Charged with Hellhoffite.**—The principle employed in using high explosives as a charge for projectiles is applicable to explosives of the Sprengel class as well as to those already enumerated. As applied to this special class of explosives, it consists in placing the ingredients in the shell in separate vessels of glass, porcelain, or similar material, which are strong enough to resist the jolts and jars incident to transportation and handling, but which are broken by the shock of discharge in the gun; or it may be done by dividing the shell into compartments by suitable diaphragms. When the first method is used the vessels are encased in rubber, felt, or other elastic material before being introduced into the projectile.

In his earlier experiments with hellhoffite, Gruson placed the nitric acid in the head of the projectile, and the dinitrobenzene in the base. When explosion after penetration was required the ingredients were placed in reverse order, and a delay-action fuse in the base retarded the operation of the mixture until the point of greatest penetration had been attained.

In 1883 six 15-cm. shell, each containing 1.1 kg. of hellhoffite, were fired against a parapet. The damage done amounted to four times that effected by a like number of shell charged with gunpowder and fired under similar conditions. In 1884 twelve 15-cm. Gruson shell, each containing 1.9 kg. of hellhoffite, were fired at Palmanova with 1.2 kg. of gunpowder, and four rounds with 1.4 kg. of powder. Subsequently three 24-cm. shell charged with 5.53 kg. of the same explosive were fired with 4.2 kg. of powder. There were no premature explosions, but, aside from the inaccuracy of the projectiles, the effect was less than that of similar shell charged with guncotton, although greater than that of shell charged with gunpowder.

**Experiments with Shell Charged with Mélinite.**—During recent years the attention of all military powers has been attracted by the experiments with mélinite, conducted by the French Government, but in the majority of trials the authorities have succeeded in maintaining a strict secrecy. The results of the *Belliqueuse* experiments are well known. Although but little effect was produced by the mélinite-charged shell on the armored portions of the vessel, the destruction wrought by the shells which penetrated the unarmored parts was so terrible as to cause the naval experts to recommend that all unfinished vessels be protected by complete armor in order to resist the fire of all such projectiles.

The fire directed against the *Belliqueuse* was from 14-cm. and 16-cm. guns of the model of 1881, and the shell, weighing 66 and 99 pounds, were charged respectively with 6.2 and 8.8 pounds of mélinité.



Dumas-Guilin states that shell containing 33 kg. of mélinite have been fired at Bourges, and that the effect produced by mélinite shell is fully equal to that produced by the Germans with guncotton shell. Recent reports claim that mélinite shell have been repeatedly and successfully fired from high-power powder-guns, under service conditions, with velocities as high as 2000 feet per second, and it is an established fact that charges of nearly 70 pounds have been fired from 22-cm. mortars with velocities exceeding 1300 feet per second. According to Professor Munroe, from whose excellent course of lectures I have so largely borrowed in the preceding pages, we are more likely to find the high explosive for use in shell among the nitro-substitution compounds than among the nitric esters.

## LECTURE XXII.

### EXPLOSION BY INFLUENCE, OR SYMPATHETIC EXPLOSION.

IN considering the various theories which have been proposed by investigators in explanation of the phenomena attending the explosion of different explosive substances, the subtlety and plausibility of their reasoning together with the originality and delicacy of their experiments, lead us to overlook certain well-known and generally accepted facts.

Both explosion and detonation may be considered as but different phases of the common and daily occurring phenomenon known as combustion, in which the element of time varies between very wide limits.

We are well aware of the fact that the application of heat, directly or indirectly, is the principal means of producing an explosion, and this is equally true in the case of combustion and detonation. It has been pointed out that the mode of producing the heat also exercises a very important influence upon the nature or the explosive reaction—so much so, in fact, that it is possible to cause the same explosive to burn, explode, or detonate, according to the circumstances attending the transformation.

**Explosion by Influence, or Sympathetic Explosion.**—Detonation has been defined as the instantaneous explosion of the whole mass of a body, and it is a peculiarity of a detonating explosion, that when produced in a body it *may* induce a similar explosion in another portion of the same body, either when in contact with it, or even when only near it, but not in contact. In fact, it may induce such an explosion when separated from the second portion by means of a glass or metal plate, or even a mass of water, so that no heated or ignited particles can be projected from one to the other.

This secondary explosion has been termed *sympathetic explosion*, or *explosion by influence*, and has been deeply investigated by several eminent scientists.

**Abel's Investigations.**—Abel has shown that not only would a detonating body cause the detonation of another mass of the same body, but that it would cause also the detonation of other bodies. For instance, by detonating mercury fulminate in contact with guncotton or nitroglycerine these bodies were also readily detonated. Only a small quantity of fulminate was required, 0.32 of a gramme (5 grains), when confined in a sheet-metal cap and placed in direct contact with the nitroglycerine or compressed guncotton, being sufficient to cause the detonation of the latter.

He found that a mass of nitroglycerine by its explosion would cause the explosion of another mass of nitroglycerine, even though both were immersed in water. His experiments further showed that a peculiar kind of initial detonation or explosion was required in order to cause the detonation of another explosive. For instance, while the detonation of guncotton would cause the detonation of nitroglycerine in close proximity to it, the detonation of nitroglycerine would not cause the detonation of guncotton.

This shows that this property of causing detonation does not depend alone upon the force of the detonator, for we know that nitroglycerine is more powerful than guncotton. Again, silver fulminate, which explodes more violently and sharply than mercury fulminate, and nitrogen iodide, and nitrogen chloride, which are the most violent explosives we possess, are very much less efficient in causing detonation than mercury fulminate. In the course of his investigations, Abel was led to the conclusion "that a particular explosion or detonation may possess a power of determining, at the instant of its occurrence, similar violent explosions in distinct masses of the same material, or in contiguous explosive bodies of other kinds, which power is independent of or auxiliary to the distinct operation of mechanical force developed by that explosion; that as a particular musical vibration will



establish synchronous vibrations in particular bodies while it will not affect others, and as a chemical change may be wrought in a body by its interception of only particular waves of light, so some kinds of explosions or powerful vibratory impulses may exert a disturbing influence over the chemical equilibrium of certain bodies, resulting in their sudden disintegration, which other explosives that develop equal or greater mechanical force are powerless to exercise.

**Abel's Theory of Synchronous Vibrations.**—Abel offers the following as being the most satisfactory explanation of the remarkable differences pointed out:

“The vibrations produced by a particular explosion, if synchronous with those which would result from the explosion of a neighboring substance, which is in a state of high chemical tension, will, by their tendency to develop those vibrations, either determine the explosion of that substance, or at any rate greatly aid the disturbing effect of mechanical force suddenly applied; while in the case of another explosion which produces vibrations of a different character, the mechanical force applied by its agency has to operate with little or no aid; greater force or more powerful detonation must, therefore, be applied in the latter instance, if the explosion of the same substance is to be accomplished.”

That vibrations will induce the decomposition of chemical compounds whose atoms are in a state of unstable equilibrium is a fact too well established in science to be dwelt upon.

**Investigations of Champion and Pellet.**—This theory was examined experimentally by MM. Champion and Pellet. They took a tube seven metres long, made in two lengths and joined by a paper band. Small quantities of nitrogen iodide were placed in each end, and when one was exploded it immediately caused the explosion of the iodide at the other end; but if the paper band connecting the two lengths was removed, the second explosion did not occur. By a suitable apparatus it was shown that the effect produced was not due to the action of a puff of air, but to vibrations of the air such

as are caused by a sounding body. When nitrogen iodide was attached to the strings of a double bass and the string was bowed, the iodide exploded when placed on the string giving the highest rate, but not when on the two lower strings. The lowest number of vibrations which would cause explosion was found to be thirty per second.

Similar results were obtained with other musical instruments. A further set of experiments was made to determine the difference between the vibrating motion excited by various detonants, and thus to account for the differences in their ability to provoke, by means of the intervening air, the explosion of other detonants placed at a distance. A series of sensitive flames was arranged, corresponding to the complete scale of G major, and 0.03 gramme of mercury fulminate excited the *a*, *c*, *e*, *f*, and *g*. A like quantity of nitrogen iodide when exploded under similar conditions produced no effect. This showed that the vibrations excited by the two explosives were very different, and also that the vibrations excited by the mercury fulminate affect flames belonging to some notes of the scale to the exclusion of others.

On exploding these substances nearer the flames than in the former experiment, while the nitrogen iodide excited only flames corresponding to the higher notes of the scale, the mercury fulminate affected them all. In these experiments it was observed that acute sounds predominate in explosions.

The same investigators took conjugate parabolic mirrors, covered their surfaces with lampblack so as to prevent the reflection and concentration of heat-rays from them, placed them 2.5 metres apart, and distributed small masses of nitroglycerine and of nitrogen iodide at different points along the line of foci. They then detonated a large drop of nitroglycerine at one of the foci, and observed that the substances placed in the corresponding conjugate focus detonated, but that the rest remained unaffected. This same line of investigation was continued by Abel, who claimed that his results tended to confirm his theory.

**Berthelot's Investigations.**—Berthelot contended that

not only were these experiments inconclusive, but, from his point of view, several of them appeared directly opposed to Abel's theory. He noted in the first place that the characteristic feature of the given musical note, which is capable of determining each variety of explosion, had never been established; that it was only below a certain note that the effects ceased to be produced; while the various explosive substances, almost without exception, proved particularly sensitive to the action of the most acute notes. Moreover, these effects ceased to be produced at distances which were incomparably less than the resonance of the chords in unison, and this fact, he claimed, proved that the detonations were functions of the intensity of the mechanical action, rather than of the character of the determining vibration. Similarly, the detonation ceased to be produced when the weight of the detonating substance was very slight, and when in consequence the mechanical energy of the shock was greatly weakened. Yet if the theory of "synchronous vibrations" were true, the specific vibratory note which determines the explosion should always remain the same. For instance, cartridges filled with dynamite No. 1 cannot be detonated by a cap containing less than 0.2 gramme of fulminate, and the detonation is assured only when the detonator contains one full gramme of the fulminate.

This, the investigator claims, establishes the fact of the existence of a direct relation between the character of the detonation and the intensity of the shock produced by one and the same detonating substance.

If it be true that guncotton will cause the detonation of nitroglycerine in consequence of the synchronism of the vibration communicated, then the effect of these substances upon each other should be reciprocal, and the failure of nitroglycerine to detonate guncotton, therefore, is due to the difference in the structure of the two substances, which plays a very important part in the transformation of the mechanical energy into work. This diversity of structure and the modifications which it causes in the transformation of the phenomena



of the shock, and the transformation of the mechanical energy into thermal energy, may be cited to explain the facts observed by Abel.

All the effects observed with nitrogen iodide may be explained by the vibration of the supports and by the friction resulting therefrom. The experiment with the conjugate mirrors may be explained by the mechanical effects resulting from the movement of the air when concentrated in the focus. Moreover, M. Lambert has shown experimentally that in the explosion of dynamite cartridges in cast-iron tubes of large diameter, regarded from the standpoint of detonation by influence, there does not appear to be any difference between the ventral segments and the nodes characteristic of the tube. To clear up this matter by eliminating the influence of the supports, and the diversity existing in the cohesion and physical structure of the solid explosive substances used, Berthelot undertook a series of experiments on the chemical stability of matter in sonorous vibration, and especially on that of gaseous bodies such as ozone and hydrogen arsenide, or liquids such as hydrogen peroxide and persulphuric acid; all of these bodies being selected from among those which decompose with the disengagement of heat, precisely as explosive substances do.

The experiments were made by enclosing the substances in glass vessels which were attached to one arm of a tuning-fork, which vibrated at the rate of one hundred single vibrations per second, or by enclosing them in a glass tube which, by means of a rubber, was made to give 7200 single vibrations per second. The substances were analyzed, and then subjected to the vibratory action for periods varying from one-half to one and one-half hours and then analyzed again. In no case had there been any notable decomposition, whence the investigator concluded that endothermous bodies were stable under the influence of sound-waves, but were decomposed under the influence of ethereal vibrations.

**Berthelot's Theory.**—From the consideration of these facts, and especially from experiments made in firing under

water, Berthelot concluded that *explosions by influence, like detonations in contact, were due to the transmission of a shock*, arising from the enormous and sudden pressure by the explosive, which is converted into heat within the explosive material itself. Thus, in the extremely rapid reaction which obtains, the pressures produced may approach to the limit which corresponds to the matter detonating in its own volume, and the commotion due to this sudden development of almost theoretical pressures can be propagated through the ground and supports as intermediaries, or through the air itself, being projected *en masse*, as has been shown in the explosion of certain powder factories and guncotton magazines, and in some of the experiments made with dynamite and compressed guncotton.

The intensity of the shock propagated, either by a column of air or a liquid or solid mass, varies with the nature of the explosive body and its mode of inflammation; it is of greater violence according as the duration of the chemical reaction is shorter and develops more gas, that is to say, a higher initial pressure and more heat, and consequently more work for the same weight of explosive material. This shock is transmitted better by solids than by liquids, better by liquids than by gases; with gases it is better, as they are more compressed. Through solids it is better propagated according to their degree of hardness. All breaks of continuity in the transmitting material tend to weaken it, especially if a softer substance is interposed. Thus it is that the use of a tube made from a goose-quill as a receiver stops the effect of mercury fulminate, while a tube or a capsule of copper transmits this effect in all its intensity.

Explosion by influence is the better propagated in a series of cartridges, according as the envelope of the first detonating cartridge is the more resisting, as it thus enables the gases to obtain a greater pressure before the covering is destroyed.

The existence of an empty space, that is to say, one filled only with air between the fulminate and the dynamite, dimin-

ishes the violence of the shock transmitted, and in consequence that of the explosion, and in general the effects of violent powders are lessened when there is no contact.

To form a full conception of the transmission by the medium of sudden pressures which produce shock, it is desirable to recall the general principle in virtue of which pressures are transmitted in a homogeneous mass equally in all directions, and are the same on any small element of the surface whatever its position. Detonations produced under water with guncotton show that this principle is equally applicable to the sudden pressures which produce explosive phenomena. But it ceases to be true when one passes from one medium to another.

If the inert chemical matter which transmits the explosive movement is fixed in a given situation like the surface of the ground, or, better still, held by the pressure of a mass of deep water, in the midst of which the first detonation is produced, the propagation of the movement in this medium will hardly be able to take place, except under the form of a wave of purely physical order, and consequently of an essentially different character from the original wave which is developed in the explosive body itself, and which is of a chemical and physical order. Whilst the first wave, which is of a chemical order, is propagated with a constant intensity, the new wave, which is of a physical order, transmits the concussion away from the explosive centre all around it with an intensity which decreases inversely as the square of the distance. In the neighborhood of the centre of the explosion the displacements of the molecules may overcome the cohesion of the mass and disperse it, or crush it by enlarging the explosion-chamber if the operation is conducted in a cavity. But at a very short distance (the magnitude of which depends on the elasticity of the surrounding medium) these movements, confused at the beginning, arrange themselves in such order as to produce a wave, properly so called.

Characterized by compressions and sudden deformations of the material, the amplitude of these oscillations depends



upon the magnitude of the initial impulse. They move with a very great rapidity, and preserve their irregularity up to the point where the continuity of the medium is interrupted; then these compressions and sudden deformations change their nature, and are transformed into a movement of impulse, that is to say, they reproduce the shock. If then they act on a new cartridge, they may determine its explosion; the shock will be otherwise weakened by the distance, and in consequence the character of the explosion may be modified. The effects diminish in this manner up to a certain point, from which the explosion ceases to produce itself. When this occurs with a second cartridge, the same series of effects will be continued from the second to the third cartridge; but this depends on the character of the explosion which the second cartridge undergoes. And thus it goes on.

Such is the theory that Berthelot offers to explain explosions by influence, and the phenomena which accompany them. It depends definitely on the production of two orders of waves, one series representing the explosive waves, properly so called, developed in the midst of the matter which detonates, and consisting of a continually reproduced transformation of chemical actions into thermal and mechanical actions, which transmit the shock to the support and to the contiguous bodies; the other being a purely mechanical and physical series, which transmits the sudden pressure equally about the centre of the concussion to the adjoining bodies and, by a singular circumstance, to a new mass of explosive material. As to the action within the original mass, he holds that the kinetic energy of the shock of the explosion (by the detonator) is transformed into heat at the point struck; the temperature of this point is thus raised to the temperature of explosion, a new shock is produced which raises the temperature of the neighboring portions to the same degree; they then explode, and the action is propagated with an ever-increasing velocity.

**Threlfall's Investigations.**—Neither Abel's theory of synchronous vibrations nor Berthelot's wave theory satisfied

Threlfall, and he therefore made an experimental and critical study of the manner in which the explosive reaction is communicated from one explosive mass to another explosive mass through a non-explosive medium. Much might be learned from a measurement of the velocity of transmission of a shock to points at small distances from the centre of explosion. This would be merely a question of experiment, and Lord Rayleigh suggested the use of a sensitive flame and revolving mirror, which would, at all events, give some idea of the sort of disturbance experienced; but Threlfall deemed it best to begin by examining cases where the results of explosion could be seen and watched. For this purpose he constructed a tank measuring a yard each way, and provided with windows in the sides. The tank was filled with water, and water-tight glass bulbs of one-half inch diameter, filled with mercury fulminate, were sunk to the depth of eighteen inches in the water, fired by electricity, and the course of the *débris* from the explosion noted. As the torpedo was suspended vertically, this *débris* had the appearance of being shot down to the bottom of the tank, not in a jet as might have been expected, but with exactly the rolling motion that smoke has in coming out of a chimney—as if, in fact, there were vortex motion of some sort.

The constancy of the downward action of the explosion suggested that it was due to the want of symmetry introduced by the neck and wires of the torpedo. Hence experiments were made in which the torpedoes were placed horizontally, and then the *débris* seemed to move with its peculiar rolling motion horizontally away from the neck. In fact, the appearance presented to the unaided eye was that of a more or less definite column of rolling white smoke shot out with great velocity, and coming to rest very rapidly when about five inches from the centre, as if acted upon with an irresistible force. Experiments were also made by exploding a charge in the centre of a Florence oil-flask, filled with red dye and immersed in the water. The dye was shot out with the *débris*, and the flash appeared to be suddenly stopped some

two or three inches outside where the flask would have been if it had not disappeared. There were, however, so many sources of misinterpretation to be feared in this method of observation that it was not continued, but the experimenter contented himself with noting the peculiar rolling motion of the dye as it was shot out.

Experiments were now made to determine if the directions of projection of the *débris* coincided with the directions of propagation of the stream of explosive energy. For this purpose a pendulum gauge was devised which was fitted to the tank, and by firing some dozen torpedoes, arranged as symmetrically as possible, he found that the indications of the gauges were nearly proportioned. Explosions were then produced in torpedoes purposely made unsymmetrical, either by having the glass too thick on one side, or by turning up the ends of the covered conducting wires, so that they entered the bulb horizontally and facing one of the gauges.

The effects now became more puzzling, but on the whole there was no question but that the gauge towards which the bulb was turned suffered most. In fact, the direction taken by the streams of explosive energy appeared to coincide with the directions of projection of *débris*, and with the direction foretold from the initial conditions. The experiments were repeated at various distances, and in various manners with more or less compressed charges, and with variations in the position of the firing-point. The pendulum readings were on the whole proportional to the direction of explosion as foretold from the initial conditions.

Of course, in some few cases, there were unexpected actions on the gauges, but this was hardly avoidable, since the previous experiments had shown how small a change in initial conditions could lead to great variations in the result. The position of the firing-point was the least satisfactory part of the experiments; most of the failures could be traced to imperfect centring of the firing-point; about ten per cent of the experiments failed to travel on the paths laid out for them. These experiments leave little doubt that the direc-



tion in which the maximum explosive effect is transmitted will in a great measure depend on the initial arrangement of surrounding obstacles; at all events, when the explosion is caused by fulminate of mercury and small charges are used. In fact, the shock of an explosion must be transmitted in one or more of three different ways:

**Threlfall's Theory.**—As the result of his investigations, Threlfall concluded that the shock of an explosion must be transmitted in one of three ways, or by a combination of two or of all three ways, as follows:

1. By actual bodily motion of the products of explosion through the surrounding medium, either alone or becoming more and more mixed up with the medium itself, which is thereby set in motion.

2. By an undulating motion set up in the medium.

3. By vortex-ring motion.

In the explosion of gunpowder and other slow explosives the energy is transmitted chiefly by 1 and 2. The distance to which a considerable quantity of the energy may be conveyed by means of waves of comparatively great amplitude is in some cases remarkably great. This is evidenced by the effects produced by the explosion of powder-magazines.

In the case of the fulminates of mercury and silver, gun-cotton and nitroglycerine, that is, explosives of the class examined under water, the effect falls off very rapidly with the distance, and in water, at all events, is of a directed character. This would point to the third mode of transmission being in these cases of some importance, and if we consider the way in which the products of explosion escape, we shall find that the conditions for the production of vortex motion do exist. Let there be a sphere of mercury fulminate fired from its geometrical centre, then, by Vieille's experiments on the time of explosion, it seems likely that the outer portions of the fulminate will be decomposed before they are removed to any appreciable distance from their original positions.

We shall therefore have a sudden expansion in all directions, caused by the increase in volume of the explosive

substance during the explosion. There seems no reason why, under perfectly symmetrical conditions, the expansion should not go on as it began until the cooling of the sphere of hot gases becomes so marked as to prevent further expansion. If the conditions, however, are not such as to allow of symmetrical expansion, which occurs in practice, then we shall have the bounding surface of the explosion-gases more curved in some places than in others, that is, the strain will be greater at some parts than at others, and in fact may become so great at points of greatest curvature as to lead to a state of "breakdown." In other words, the compressed gases in this case escape, not by gradual expansion, but by jets, from points whose positions are fixed by the conditions of explosion. In these jets we should have the necessary and sufficient conditions for the establishment of vortex motion. If vortex motion were set up, then it seems likely that much greater effects might be transmitted in some directions than in others, though at considerable distances the effects would tend to become uniform in all directions. Threlfall believes that this view of the actions of explosions will enable us to explain several difficulties occurring in the interpretation of Abel's experiments. Among these are: the want of correspondence between the explosive actions, as measured by the effect produced on copper plates, and the effects produced in causing explosions; the apparent capriciousness of explosions of the more violent kinds; and, finally, the production of explosions by influence.

The investigations of these eminent scientists, and the theories advanced by them in explanation of the observed phenomena, have been ably reviewed by Professor C. E. Munroe, Chemist to the U. S. Naval Torpedo Corps. While recognizing the plausibility of the theory advanced by Berthelot, and admitting that his views are in a measure supported by experiments, Professor Munroe is unwilling to accept this theory in its entirety. In fact, he rather inclines to Abel's theory of "synchronous vibrations." Touching the investigations of MM. Champion and Pellet, the only

points noted refer to the explosive substance used in their experiments—nitrogen iodide—and the peculiar conditions under which the experiment with mirrors was performed. In the first case, the only cause for surprise or wonder is that the investigators were able to find a string that would vibrate sufficiently slowly not to fire the iodide; while in their efforts to establish the theory of synchronous vibrations by the mirror experiments, they proceeded to coat the surfaces of the mirror with a material (lampblack) which would absorb the vibrations which, upon this theory, would be most active in producing the desired effect.

In conclusion, he claims that if the synchronous vibrations can be disproved at all by experiment, then Abel himself has contributed the strongest evidence against it. In the light of what has been published on the subject, there is sufficient reason for hesitation in accepting Abel's theory. On the other hand, if the vortex motion be accepted, several otherwise apparently inexplicable phenomena are readily accounted for. At present, therefore, it would seem that the capriciousness of explosions, such as was exemplified in the Bremerhaven disaster, cannot be explained upon any theory of uniform wave motion, but, on the other hand, are readily explicable upon the hypothesis of the coexistence of two states of propagation, that of wave motion and that of vortex motion.





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